A TEXT-BOOK

OF

ORGANIC CHEMISTRY

RICHTER

ANSCHÜTZ

SMITH

VOLUME II OF THIS WORK, THE AROMATIC SERIES, IS IN RAPID PREPARATION AND WILL BE PUBLISHED DURING 1899.

VICTOR VON RICHTER'S

ORGANIC CHEMISTRY

OR

CHEMISTRY

OF THE

CARBON COMPOUNDS

EDITED BY

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AUTHORIZED TRANSLATION

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Third American from the Eighth German Edition

VOLUME I

CHEMISTRY OF THE ALIPHATIC SERIES

WITH ILLUSTRATIONS

PHILADELPHIA
P. BLAKISTON'S SON & CO.
1012 WALNUT STREET
1899

79201

WM. F. FELL & CO.,
ELECTROTYPERS AND PRINTERS,
1220-24 SANSOM STREET,
PHILADELPHIA.

PREFACE

TO THE

THIRD AMERICAN EDITION.

In presenting this translation of the eighth German edition of v. Richter's "Organic Chemistry" the writer has little to add to what has previously been expressed in the prefaces to the preceding American editions of this most successful book. The student of the present edition will, however, very quickly discover that the subject matter, so ably edited by Professor Anschütz, is vastly different from that given in the earlier editions. Indeed, the book has sustained very radical changes in many particulars, and certainly to its decided advantage. The marvelous advances in the various lines of synthetic organic chemistry have made many of the changes in the text absolutely necessary, and for practical reasons it has seemed best to issue this new edition in two volumes.

Eminent authorities, such as Profs. v. Baeyer, E. Fischer, Waitz, Claisen, and others, have given the editor the benefit of their supervision of chapters relating to special fields of investigation in which they are the recognized authorities.

The translator here acknowledges his great indebtedness to his publishers, P. Blakiston's Son & Co., for their constant aid in his work, as well as to Messrs. Wm. F. Fell & Co., for the care they have taken and the skill they have displayed in the composition of what will generally be admitted to be a difficult piece of typography.

PREFACE TO SECOND EDITION.

The present American edition of v. Richter's "Organic Chemistry" will be found to differ very considerably, in its arrangement and size, from the first edition. The introduction contains new and valuable additions upon analysis, the determination of molecular weights, recent theories on chemical structure, electric conductivity, etc. The section devoted to the carbohydrates has been entirely rewritten, and presents the most recent views in regard to the constitution of this interesting group of compounds. The sections relating to the trimethylene, tetramethylene, and pentamethylene series, the furfurane, pyrrol, and thiophene derivatives, have been greatly enlarged, while the subsequent chapters, devoted to the discussion of the aromatic compounds, are quite exhaustive in their treatment of special and important groups. Such eminent authorities as Profs. Ostwald, von Baeyer, and Emil Fischer have kindly supervised the author's presentation of the material drawn from their special fields of investigation.

The characteristic features of the first edition have been retained, so that the work will continue to be available as a text-book for general class purposes, useful and reliable as a guide in the preparation of organic compounds, and well arranged and satisfactory as a reference volume for the advanced student as well as for the practical chemist.

The translator would here express his sincere thanks to Prof. v. Richter, whose hearty cooperation has made it possible for him to issue this translation so soon after the appearance of the sixth German edition.

PREFACE

TO THE

FIRST AMERICAN EDITION.

The favorable reception of the American translation of Prof. von Richter's "Inorganic Chemistry" has led to this translation of the "Chemistry of the Compounds of Carbon," by the same author. In it will be found an unusually large amount of material, necessitated by the rapid advances in this department of chemical science. The portions of the work which suffice for an outline of the science are presented in large type, while in the smaller print is given equally important matter for the advanced student. Frequent supplementary references are made to the various journals containing original articles, in which details in methods and fuller descriptions of properties, etc., may be found. The volume thus arranged will answer not only as a text-book, and indeed as a reference volume, but also as a guide in carrying out work in the organic laboratory. To this end numerous methods are given for the preparation of the most important and the most characteristic derivatives of the different classes of bodies.

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VIII. HEXAHYDRIC AND POLYHYDRIC ALCOHOLS AND THEIR OXIDATION PRODUCTS.

ANIMAL SUBSTANCES OF UNKNOWN CONSTITUTION.

ABBREVIATIONS.

A. = Liebig's Annalen der Chemie. Spl. = Supplementband.
A. ch. phys. or A. chim. phys. = Annales de chimie et de physique.
Arch. exp. Path. = Schmiedeberg's Archiv für experimentelle Pathologie und Pharmakologie.
Arch. f. d. ges. Phys. = Pflüger's Archiv für die gesammte Physiologie.
B. = Berichte der deutschen chemischen Gesellschaft. R. = Referate.
Bull. soc. ch. = Bulletin de la société chimique de Paris.
C. or Ch. C. = Chemisches Centralblatt.
Ch. Zt. or Chem. Zt. = Chemiker-Zeitung.
C. r. = Comptes rendues des séances de l'Académie des sciences.
D. R. P. = Deutsches Reichspatent.
J. = Jahresbericht für die Fortschritte der Chemie.
J. Ch. S. or J. ch. S. or Chem. Soc. = Journal of the Chemical Society.
J. pr. Ch. or J. pr. Ch. N. F. = Journal für praktische Chemie. Neue Folge.
Ladenburg's Handw. = Ladenburg's Handwörterbuch für Chemie.
F. N. Hdw. or Hdw. = Fehling's Handwörterbuch für Chemie.
Pharmac. Centralhalle = Pharmaceutische Centralhalle.
Phil. Mag. = Philosophical Magazine.
Pogg. A. or Wied. A. = Poggendorf's Annalen der Physik und Chemie, herausgegeben von Wiedemann.
R. Meyer's J. or R. M. J. = Richard Meyer's Jahrbuch der Chemie.
Wied. A. = Pogg. A.
Wien. Monatsh. = Monatsheft für Chemie (Vienna).
Z. anal. Ch. = Fresenius' Zeitschrift für analytische Chemie.
Z. f. anorg. Ch. = Zeitschrift für anorganische Chemie.
Z. f. Kryst. = Groth's Zeitschrift für Krystallographie und Mineralogie.
Z. phys. Ch. = Ostwald's Zeitschrift für physikalische Chemie.
Z. physiol. Ch. = Hoppe-Seyler's Zeitschrift für physiologische Chemie.

A TEXT-BOOK

OF

ORGANIC CHEMISTRY.

INTRODUCTION.

While inorganic chemistry was primarily developed through the investigation of minerals, and was in consequence termed *mineral chemistry*, it may be said that the development of *organic* chemistry was due to the study of products resulting from the alteration of plant and animal substances. About the close of the last century Lavoisier demonstrated that, when the organic substances present in vegetable and animal organisms were burned, carbon dioxide and water were always formed. It was this chemist also who showed that the component elements of these bodies, so different in properties, were generally carbon, hydrogen, and oxygen, to which sometimes—especially in animal substances—nitrogen was added. Lavoisier further gave utterance to the opinion that peculiarly constituted atomic groups, or radicals, were to be accepted as present in organic substances; while the mineral substances were regarded by him as the direct combinations of single elements.

As it seemed impossible, for a long time, to prepare organic bodies from the elements synthetically, the opinion prevailed that there existed an essential difference between organic and inorganic substances; and this led to the distinction of the chemistry of the first as Organic Chemistry, and that of the second as Inorganic Chemistry. The prevalent opinion was, that the chemical elements in the living bodies were subject to other laws than those in the so-called inanimate nature, and that the organic substances were formed only in the organism by the intervention of a peculiar vital force, and that they could not possibly be prepared in an artificial way.

One fact sufficed to prove these rather restricted views to be unfounded. The first organic substance artificially prepared was urea

(Wöhler, 1828). By this synthesis chiefly, to which others were soon added, the idea of a peculiar force necessary to the formation of organic compounds was contradicted. All further attempts to separate organic substances from the inorganic (the chemistry of the simple and the chemistry of the compound radicals, p. 34) were futile. At present we know that these do not differ essentially from each other; that the peculiarities of organic compounds are dependent solely on the nature of their essential constituent, Carbon; and that all substances belonging to plants and animals can be artificially prepared from the elements. *Organic Chemistry* is, therefore, the *chemistry of the carbon compounds*. Its separation from the chemistry of the other elements is demanded by practical considerations; it is occasioned by the very great number of carbon compounds (about 60,000. See B. **29**, 607), which far exceed those of any other known element. The carbon atoms unite readily with each other to form open and closed rings or chains. This property carbon possesses to a greater degree than any other element. The numerous existing carbon nuclei in which atoms or atomic groups of other elements have entered in the formation of organic derivatives have arisen in this manner.

The impetus given to the study of the compounds of carbon has not only brought new industries into existence, but it has caused the rapid development of others of like importance to the growth and welfare of the nation.*

The advances of organic chemistry are equally important in the investigation of the chemical processes in vegetable and animal organisms. This is the office of *Physiological Chemistry*.

COMPOSITION OF CARBON COMPOUNDS.

ELEMENTARY ORGANIC ANALYSIS.

Most carbon compounds occurring in vegetables and animals consist of carbon, hydrogen, and oxygen. This was demonstrated by Lavoisier, the founder of organic elementary analysis. Many, also, contain nitrogen, and on this account these elements are termed *Organogens*. Sulphur and phosphorus are present in some naturally occurring substances. Almost all the elements, non-metals and metals, may be artificially introduced as constituents of carbon compounds in direct union with carbon. The number of known carbon compounds is exceedingly great. The general procedure, therefore, of isolating the several compounds of a mixture, as is done in mineral chemistry in the separation of bases from acids, is impracticable. The mixtures occurring in vegetable and animal bodies are only separated by special methods. The task of elementary organic analysis is to determine,

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* Wirthschaftliche Bedeutung chemischer Arbeit, von H. Wichelhaus, 1893.

qualitatively and quantitatively, the elements of a carbon compound after it has been obtained in a pure state and characterized by definite properties, crystalline form, specific gravity, melting point, and boiling point. Simple practical methods for the direct determination of oxygen do not exist. Its quantity is usually calculated by difference, after the other constituents have been found.

DETERMINATION OF CARBON AND HYDROGEN.

The presence of carbon in a substance is shown by its charring when ignited away from air. Ordinarily its quantity, as also that of the hydrogen, is ascertained by combustion. The substance is mixed in a glass tube with copper oxide and heated. The cupric oxide gives up its oxygen, is reduced to metallic copper, while the carbon burns to carbon dioxide, and the hydrogen to water. In quantitative analysis, these products are collected in separate vessels, and the increase in the weight of the latter determined. Carbon and hydrogen are always simultaneously determined in one operation. The details of the quantitative analysis are fully described in the text-books of analytical chemistry.* It is only necessary here, therefore, to outline the methods employed. Liebig deserves much credit for his elaboration of these methods (Pogg. A. (1831), **21**, 1).

As a usual thing, the combustion is effected by the aid of copper oxide or fused and granulated lead chromate in a tube of hard glass, fifty to sixty centimetres long (depending upon the greater or less volatility of the organic body). Substances, which burn with difficulty, should be mixed with finely divided cupric oxide, finely divided lead chromate, or with cupric oxide to which potassium bichromate has been added.

The combustion tube is drawn into a point, and the contracted end given a bayonet-shape (Liebig), or it is open at both ends (Glaser, A. Suppl. **7**, **213**). Cloëz has also suggested the use of an iron tube (Z. anal. Ch. **2**, 413).

The tube is placed in a suitable furnace, which formerly was heated by a charcoal fire, but at present gas is exclusively employed (A. W. Hofmann, A. **90**, 235; **107**, 37; Erlenmeyer, Sr., A. **139**, 70; Glaser, *l. c.*; Anschütz and Kekulé, A. **228**, 301; B. **25**, 2723).

When the tube has been filled, the open end is attached to an apparatus designed to collect the water produced in the combustion. The substances used to retain the moisture are:

1. A U-tube filled with carefully purified calcium chloride, which has been dried at 180° C.

2. Pure, concentrated sulphuric acid contained in a spiral-shaped tube, or pumice fragments, dipped in the acid, and placed in a U-tube (Mathesius, Z. anal. Ch. **23**, 345).

3. Pellets of glacial phosphoric acid, contained in a U-tube. The vessel intended to receive the water is in air-tight connection with the apparatus designed to absorb the carbon dioxide. For the latter purpose a Liebig bulb was formerly employed, but later that of Geissler came into use, and very recently Delisle (B. **24**, 271) has recommended a similar absorption vessel. In commercial work U-tubes, filled with

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* Anleitung zur Analyse organischer Körper, J. Liebig. 2. Aufl. 1853. Quantitative chemische Analyse, R. Fresenius. 6. Aufl., Bd. 2, S. 1–110. Chemische Analyse organischer Stoffe, von Vortmann.

granulated soda-lime, are substituted for the customary bulbs (Mulder, Z. anal. Ch. 1, 2).

When the combustion is finished, oxygen free from carbon dioxide is forced into the combustion-tube, or drawn through it by means of an aspirator; air being substituted for it later, with the precaution that the pieces of apparatus serving to dry the oxygen and air are filled with the same material which was used in the water-absorbing tubes. As soon as the entire system is filled with air, disconnect the several pieces of apparatus and weigh them separately. The increase in weight of the apparatus in which the water was collected represents the water resulting from the combustion of the weighed substance, and the increase in weight of the bulbs the quantity of carbon dioxide. Knowing the composition of water and carbon dioxide. the quantity of carbon and hydrogen contained in the burnt substance can readily be calculated in percentage.

Fig. 1 represents one end of a combustion furnace of the type devised by Kekulé and Anschütz (A. 228, 301). In it lies the combustion tube V. This is connected with a Klinger calcium chloride tube A; B is a Geissler potash-bulb, joined to a U-tube C, one limb of which is filled with pieces of stick potash, and the other with calcium chloride. G represents mica-plates; these permit of a careful observation of the flame. E is a section of the iron tube in which the combustion tube V rests. T is a side clay-cover placed over the mica-strips. D is a clay-cover for the top. R is the gutter into which the gas-pipe, bearing the burners, can be placed or from which it can be removed for repair, etc.

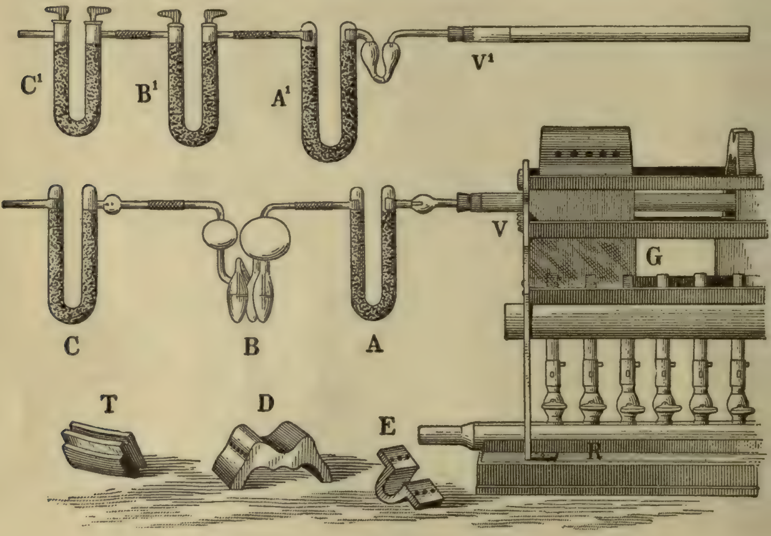

FIG. 1.

Fig. 1 also shows, above the combustion tube, the anterior portion of a similar tube, provided with a Bredt and Posth (A. 285, 385) calcium chloride tube, in which the movement of a drop of water enables the analyst to determine the rapidity of the combustion. B^1 is a U-tube filled with soda-lime and provided with ground glass stoppers. C^1 is a similar tube, filled one-half with soda-lime and one-half with calcium chloride.

Instead of oxidizing the organic substance with the combined oxygen of cupric oxide or lead chromate the method of Kopfer may be substituted. In this platinum black is made to carry free oxygen to the vapors of the substance. A much shorter and more simple combustion furnace may then be employed. The method is adapted to the combustion of compounds containing the halogens (Z. anal. Ch. **17**, **1**). Dudley has found that a platinum tube, having a layer of granular manganic oxide in the anterior part, is of great service when substances are placed in boats and exposed to combustion (B. **21**, 3172).

When *nitrogen* is present in the substances burned, oxides of it are sometimes produced; these must be reduced to nitrogen. This may be accomplished by conducting the gases of the combustion over a layer of metallic copper filings, or a copper spiral, placed in the front portion of the combustion tube. The latter, in such cases, should be a little longer than usual. The copper is previously reduced in a current of hydrogen, then ignited, when it often includes hydrogen, which subsequently becomes water. To remedy this, the copper after reduction in a current of hydrogen is heated in an air-bath or, better, in a current of carbon dioxide or to 200° in a vacuum. Its reduction by the vapors of formic acid or methyl alcohol is more advantageous; this may be done by pouring a small quantity of these liquids into a dry test tube and then suspending in them the roll of copper heated to redness; copper thus reduced is perfectly free from hydrogen.

It is generally unnecessary to use a copper spiral when the combustions are executed in open tubes, because nitric oxide (NO) only is produced, and this passes through the caustic potash unabsorbed (B. **22**, 3066, note).

In the presence of *chlorine*, *bromine* or *iodine*, halogen copper compounds (CuX) arise. These are somewhat volatile and pass over into the calcium chloride tube. The placing of a spiral of copper or silver foil in the front part of the tube will obviate this. When the organic compound contains *sulphur* a portion of the latter will be converted into sulphur dioxide, during the combustion with cupric oxide. This may be combined by introducing a layer of lead peroxide (Z. anal. Ch. **17**, **1**). Or lead chromate may be substituted for the cupric oxide. This would convert the sulphur into non-volatile lead sulphate. In the combustion of organic salts of the alkalies or earths, a portion of the carbon dioxide is retained by the base. To prevent this and to expel the CO_2, the substance in the boat is mixed with potassium bichromate or chromic oxide (B. **13**, 1641).

When carbon alone is to be determined this can be effected, in many instances, in the wet way, by oxidation with chromic acid and sulphuric acid (Messinger, B. **21**, 2910; compare A. **273**, 151).

DETERMINATION OF NITROGEN.

In many instances, the presence of nitrogen is disclosed by the odor of burnt feathers when heat is applied to the compounds under examination. Many nitrogenous substances yield ammonia when heated with alkalies (best with soda-lime). A simple and very delicate test for the detection of nitrogen is the following: Heat the substance under examination in a test tube with a small piece of sodium or potassium. When the substance is explosive, add dry soda. Cyanide of potash, accompanied by slight detonation, is the product. Treat the residue with water; to the filtrate add ferrous sulphate, containing a ferric salt, and a few drops of potassium hydroxide, then apply heat and add an excess of hydrochloric acid. An undissolved, blue-colored precipitate (Prussian blue), or a bluish-green coloration, indicates the presence of nitrogen in the substance examined.

Nitrogen is determined quantitatively: (1) as nitrogen, by the method of Dumas; (2*a*) as ammonia, by the ignition of the material with soda-lime (method of Will and Varrentrap); (*2b*) as ammonia, by heating the substance with sulphuric acid according to the directions of Kjeldahl.

1. Method of Dumas.—The substance, mixed with cupric oxide, is burned in a tube of hard-glass in the anterior end of which is a layer of metallic copper. The latter serves for the reduction of the oxides of nitrogen. The tube is filled with carbon dioxide, obtained by heating either dry, primary sodium carbonate or magnesite, contained in the posterior and closed end of the tube. It can also be filled from a carbonic acid apparatus of the type recommended by Kreusler (Z. anal. Ch. **24**, 440). In the latter case an open tube is used. When necessary the carbon dioxide is dried by passing it through sulphuric acid. A more practicable procedure consists in evacuating the tube, previous to the combustion, by aid of an air-pump, filling in each time with carbon dioxide (A. **233**, 330, note), or the air may be removed by means of a mercury pump (Z. anal. Ch. **17**, 409).

When the combustion is ended, again apply heat to another part of the sodium carbonate layer, to insure the removal of all the nitrogen from the tube and its entrance into the graduated tube or azotometer, which may have one of a variety of forms (Zulkowsky, A. **182**, 296; B. **13**, 1099; Schwarz, B. **13**, 771; Ludwig, B. **13**, 883; H. Schiff, B. **13**, 885; Staedel, B. **13**, 2243; Groves, B. **13**, 1341; Ilinski, B. **17**, 1348). The potassium hydroxide in the graduated vessel absorbs all the disengaged carbon dioxide, and only pure nitrogen remains.

Given the volume V_t of the gas, the barometric pressure p and the tension s of the potassium hydroxide (Wüllner, Pogg. A. **103**, 529; **110**, 564) at the temperature t of the surrounding air, the volume V_0 at 0° and 760 mm. may be easily deduced:

$$V_0 = \frac{V_t\ (p - s)}{760\,(1 + 0.003665\,t)}.$$

Multiply V_0 by 0.0012562, the weight of 1 c.c. of nitrogen at 0° and 760 mm., and the product will represent the weight in grams of the observed gas volume:

$$G = \frac{V_t\ (p - s)}{760\,(1 + 1.003665\,t)} \times 0.0012562.$$

The percentage of nitrogen in the substance analyzed can easily be calculated from this quantity.

Instead of reducing the observed gas volume V, from the observed barometric pressure and the temperature at the time of the experiment, to the normal pressure of 760 mm. and the temperature of 0°, the reduction may be more readily effected by comparing the observed volume of gas or vapor with the expansion of a normal gas-volume (100) measured at 760 mm. and 0°. For this purpose employ the equation $V_0 = V.\frac{100}{v}$, in which v represents the changed normal volume (100). The apparatus recommended by Kreusler (B. **17**, 30) and Winkler (B. **18**, 2534), or even the Lunge (B. **18**, 2030; **23**, 440; **24**, 1656, 3491; J. A. Müller, B. **26**, R. 388) nitrometer will answer very well for this purpose, or the nitrogen may be collected in a *gas-baroscope* (B. **27**, 2263).

Frankland and Armstrong conduct the combustion in a vacuum, and dispense with the layer of metallic copper in the anterior portion of the tube. If any nitric oxide is formed it is collected together with the nitrogen, and is subsequently removed by absorption (B. **22**, 3065).

Consult the Z. anal. Ch. **17**, 409; E. Pflüger, *ibid.*, 18, 296; and Jannasch and V. Meyer, A. **233**, 375 for methods by which carbon, hydrogen, and nitrogen are determined simultaneously.

See Gehrenbeck (B. **22**, 1694) when a method is desired for the simultaneous estimation of nitrogen and hydrogen in cases where the carbon was determined in the wet way.

For the simultaneous determination of carbon and nitrogen, see Klingemann, A. **275**, 92.

2. **Method of Will and Varrentrap.**—When most nitrogenous organic compounds (nitro-derivatives excepted) are ignited with alkalies, all the nitrogen is eliminated in the form of ammonia gas. Mix the weighed, finely pulverized substance with soda-lime (about 10 parts), place the mixture in a combustion tube about 30 cm. in length, and fill in with soda-lime. In the open end of the tube there is placed a rubber stopper bearing a bulb apparatus, in which there is dilute hydrochloric acid. The anterior portion of the tube is first heated in the furnace, then that containing the mixture. To carry all the ammonia into the bulb, conduct air through the tube, after breaking off the point. The ammonium chloride in the hydrochloric acid is precipitated with platinic chloride, as ammonio-platinum chloride ($PtCl_4.2NH_4Cl$), the precipitate ignited, and the residual Pt weighed; 1 atom of Pt corresponds to 2 molecules of NH_3 or 2 atoms of nitrogen.

Or having placed a definite volume of acid in the apparatus, the excess after the ammonia absorption may be determined volumetrically, using fluorescein or methyl orange as an indicator.

Generally, too little nitrogen is obtained by this method. A portion of the ammonia suffers decomposition. This is avoided by adding sugar to the mixture of substance and soda-lime, and by not heating the tube too intensely (Z. anal. Ch. **19**, 91). It is also advisable to fill up the tube with soda-lime as far as is possible (Z. anal. Ch. **22**, 280).

The method of Will and Varrentrap is made more widely applicable by adding reducing substances to the soda-lime. Goldberg (B. **16**, 2549) uses a mixture of soda-lime (100 parts), stannous sulphide (100 parts), and sulphur (20 parts); this he considers especially advantageous in estimating the nitrogen of nitro- and azo-compounds. For nitrates, Arnold (B. **18**, 806) employs a mixture of soda-lime (2 parts), sodium hyposulphite (1 part), and sodium formate (1 part).

3. **Method of Kjeldahl.**—The substance is dissolved by heating it with concentrated sulphuric acid. Potassium permanganate is then added until a green color appears. This treatment decomposes the organic matter; its nitrogen is converted into ammonia. After the liquid has been diluted with water the ammonia is expelled from it by boiling with sodium hydroxide (Z. anal. Ch. **22**, 366). This method is well adapted for the determination of the nitrogen of plants and animal substances; compare urea. When estimating the nitrogen of nitro- and cyanogen compounds it will be found decidedly advantageous to add sugar, and with nitrates, benzoic acid. The addition of potassium permanganate will usually be unnecessary, while that of mercuric oxide is said to be highly advantageous (B. **18**, R. 199, 297). Pyridine and quinoline cannot be analyzed by this method (B. **19**, R. 367, 368).

The Kjeldahl method for the determination of nitrogen has rapidly become a favorite in both scientific and technical work. The simplicity of operation and of apparatus has been its chief recommendation. A number of parallel determinations can be simultaneously performed in this way. The numerous modifications of the method, which have been proposed to render it generally applicable, have not yet attained their aim and purpose.

NOTE.—The nitrogen of nitro- and nitroso-compounds can be determined indirectly with a titrated solution of stannous chloride. The latter converts the groups NO_2 and NO into the amide group, with the production of stannic chloride. The quantity of the latter is learned by titrating the excess of stannous salt with an iodine solution (Method of Limpricht, B. **11**, 40).

DETERMINATION OF THE HALOGENS, SULPHUR AND PHOSPHORUS.

Qualitative Detection: Substances containing chlorine and bromine yield, when burned, a flame having a green-tinged border. The following reaction is exceedingly delicate. A little cupric oxide is placed on a platinum wire, ignited in a flame until it appears colorless, when a little of the substance under examination is put on the cupric oxide and this heated in the non-luminous gas flame. The latter is colored an intense greenish-blue in the presence of chlorine, bromine, or iodine. More decisive is to ignite the substance in a test tube with burnt lime (free from halogens), dissolve the mass in nitric acid, and then add silver nitrate.

The presence of sulphur is often shown by fusing the substance examined with potassium hydroxide; potassium sulphide results, and produces a black stain of silver sulphide on a clean piece of silver, or by heating the substance with metallic sodium and testing the aqueous filtrate for sodium sulphide with sodium nitroprusside. In estimating sulphur and phosphorus ignite the weighed substance with a mixture of saltpeter and potassium carbonate. The resulting sulphuric and phosphoric acids are sought for by the usual methods.

Quantitative Determination: A hard glass tube, closed at one end, and about 33 cm. in length, is partly filled with calcium oxide, then the mixture of the substance with lime, followed by a layer of calcium oxide. The latter should be free of chlorine. Heat the tube in a combustion furnace; after cooling shake its contents into dilute nitric acid, filter, add silver nitrate and weigh the precipitated silver haloid.

The decomposition is easier, if we substitute for lime a mixture of lime with ¼ part sodium carbonate, or 1 part sodium carbonate, with 2 parts potassium nitrate, and in the case of substances volatilizing with difficulty, a platinum or porcelain crucible, heated over a gas lamp, may be used (A. **195**, 295 and **190**, 40). With compounds containing iodine, iodic acid is apt to form; but after solution of the mass this may be reduced by sulphurous acid. The volumetric method of Volhard (A. **190**, 1) for estimating halogens by means of ammonium sulphocyanide may be employed instead of the customary gravimetric course.

The same decomposition can also be effected by ignition with iron, ferric oxide and sodium carbonate (E. Kopp, B. **10**, 290).

The substances containing the halogens may also be burned in oxygen. The gases are conducted over platinized quartz sand, and the products collected in suitable solutions (Zulkowsky, B. **18**, R. 648).

The substances may be burned in an open combustion tube in a current of oxygen, conducting the products through a layer of pure granular lime (or soda-lime), which is placed in the same tube and raised to a red heat. Later, the lime is dissolved in nitric acid, the halogens precipitated by silver nitrate, the sulphuric acid by barium chloride and the phosphoric acid (after removal of the excess of silver by HCl) by uranium acetate. Arsenic may be determined similarly (Brügelmann, Z. anal. Ch. **15**, 1 and **16**, 1). Sauer recommends collecting the sulphur dioxide, arising in the combustion of the substance, in hydrochloric acid containing bromine (*ibid.* **12**, 178).

To determine sulphur and the halogens by the method suggested by P. Klason (B. **19**, 1910), the substance is oxidized in a current of oxygen charged with nitroso-vapors. The products of combustion are conducted over rolls of platinum foil. Consult Th. Poleck (Z. anal. Ch. **22**, 171) upon a method which is applicable for the estimation of the sulphur contained in coal gas.

A method of frequent use for the determination of the halogens, sulphur and phosphorus in organic bodies is that of Carius (Z. anal. Ch. **1**, 240; **4**, 451; **10**, 103; Linnemann, *ibid.* **11**, 325; Obermeyer, B. **20**, 2928).

The substance, weighed out in a small glass tube, is heated together with concentrated nitric acid and silver nitrate to 150–300° C., in a sealed tube, and the quantity of the resulting silver haloid (B. **28**, R. 478, 864) sulphuric acid and phosphoric acid determined. The furnace of Babo (B. **13**, 1219) is especially adapted for the heating of tubes. The results by this method are not always reliable (A. **223**, 184).

In many instances, especially when the substances are soluble in water, the halogens may be separated by the action of sodium amalgam, and converted into salts, the quantity of which is determined in the filtered liquid (Kekulé, A. Suppl. **1**, 340).

Sulphur and phosphorus can often be estimated by the wet method. The oxidation is effected by means of potassium permanganate and caustic alkali, or with potassium bichromate and hydrochloric acid (Messinger, B. **21**, 2914).

DETERMINATION OF THE MOLECULAR FORMULA.*

The elementary analysis affords the percentage composition of the analyzed substance. There remains, however, the deduction of the atomic-molecular formula.

We arrive at the simplest ratio in the number of elementary atoms contained in a compound, by dividing the percentage numbers by the respective atomic weights of the elements.

Thus, the analysis of lactic acid gave the following percentage composition :—

Carbon,	40.0	per cent.	
Hydrogen,	6.6	"	
Oxygen,	53.4	"	(by difference).
	100.0		

Dividing these numbers by the corresponding weights ($C = 12$, $H = 1$, $O = 16$), the following quotients are obtained :—

$$\frac{40.0}{12} = 3.3 \qquad \frac{6.6}{1} = 6.6 \qquad \frac{53.4}{16} = 3.3$$

Therefore, the ratio of the number of atoms of C, H and O, in the lactic acid, is as 3.3 : 6.6 : 3.3 or 1 : 2 : 1. The simplest atomic formula, then, would be CH_2O; however, it remains undetermined what multiple of this formula expresses the true composition. The lowest formula of a compound, by which is expressed the ratio of the atoms of other elements to those of the carbon atoms, is an *empiric formula*. Indeed, we are acquainted with different substances having the empiric formula CH_2O, for example oxymethylene, CH_2O, acetic acid, $C_2H_4O_2$, lactic acid, $C_3H_6O_3$, grape sugar, $C_6H_{12}O_6$, etc.

With compounds of complicated structure, the derivation of the

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* Die Bestimmung des Moleculargewichts in theoretischer und practischer Beziehung, von K. Windisch, 1892.

simplest formula is, indeed, unreliable, because various formulas may be deduced from the percentage numbers by giving due regard to the possible sources of error in observation. The true molecular formula, therefore, can only be ascertained by some other means. Three courses of procedure are open to us. First, the study of the chemical reactions, and the derivatives of the substance under consideration. Second, the determination of the vapor density of volatile substances. Third, determining certain properties of the solutions of soluble substances.

(1) *Determination of the Molecular Weight by the Chemical Method.*

This is applicable to all substances. It is generally very complicated, and does not invariably lead to definite conclusions. It consists in preparing derivatives, analyzing them and comparing their formulas with the supposed formula of the original compound. The problem becomes simpler when the substance is either a base or an acid. Then it is only necessary to prepare a salt, determine the quantity of metal combined with the acid, or of the mineral acid in union with the base, and from this calculate the equivalent formula. A few examples will serve to illustrate this.

Prepare the silver salt of lactic acid (the silver salts are easily obtained pure, and generally crystallize without water) and determine the quantity of silver in it. We find 54.8 per cent. of silver. As the atomic weight of silver $= 107.7$, the amount of the other constituent combined with one atom of Ag in silver lactate, may be calculated from the proportion—

$$54.8 : (100 - 54.8) : : 107.7 : x$$
$$x = 89.0.$$

Granting that lactic acid is monobasic, that in the silver salt one atom of hydrogen is replaced by silver, it follows that the molecular weight of the free (lactic) acid must $= 89 + 1 = 90$. Consequently, the simplest empiric formula of the acid, $CH_2O = 30$, must be tripled. Hence, the molecular formula of the free acid is $C_3H_6O_3 = 90$:

$C_3 = 36$, ... 40.0
$H_6 = 6$, ... 6.7
$O_3 = 48$, ... 53.3

In studying a base, the platinum double salt is usually prepared. The constitution of these double salts is analogous to that of ammonio-platinum chloride—$PtCl_4.2(NH_3HCl)$—the ammonia being replaced by the base. The quantity of platinum in the double salt is determined by ignition, and calculating the quantity of the constituent combined with one atom of Pt (198 parts). From the number found, subtract six atoms of chlorine and two atoms of hydrogen, then divide by two; the result will be the equivalent or molecular weight of the base.

Or, the substance is subjected to reactions of various kinds, *e.g.*, the substitution of its hydrogen by chlorine. The simplest formula of acetic acid, as described above, is CH_2O. By substitution three acids can be obtained from acetic acid. These, upon treatment with nascent hydrogen, revert to the original acetic acid. They are—

$C_2H_3ClO_2$—monochloracetic acid,
$C_2H_2Cl_2O_2$—dichloracetic acid, and
$C_2HCl_3O_2$—trichloracetic acid.

Consequently, there must be three replaceable hydrogen atoms in the acid. This would lead us to the formula $C_2H_4O_2$ for it.

Knowing the molecular value of an analyzed compound, it will often be necessary to multiply its *empiric* formula to obtain one which will express the number of atoms contained in the molecule. This will be the *empiric molecular formula*.

(2) *Determination of the Molecular Weight from the Vapor Density.*

This method is limited to those substances which can be gasified and volatilized without suffering decomposition. It is based upon the law of Avogadro, according to which equal volumes of all gases and vapors at like temperature and like pressure contain an equal number of molecules (see v. Richter's Inorganic Chemistry). The molecular weights are, therefore, the same as the specific gravities. As the specific gravity is compared with $H = 1$, but the molecular weights with $H_2 = 2$, we ascertain the molecular weights by multiplying the specific gravity by two. Should the specific gravity be referred to air $= 1$, then the molecular weight is equal to the specific gravity multiplied by 28.86 (since air is 14.43 times heavier than hydrogen).

	Molecular Weight.		Specific Gravity.	
Air, ...	—	—	14.43	1
Hydrogen, ...	H_2	$= 2$	1	0.0693
Oxygen, ...	O_2	$= 31.92$	15.96	1.1060
Water, ...	H_2O	$= 17.96$	8.98	0.622
Methane, ...	CH_4	$= 15.97$	7.98	0.553

The results arrived at by the chemical method, by transpositions, and those obtained by the physical method, by the vapor density—are always identical. Experience teaches this. If a deviation should occur, it is invariably in consequence of the substance suffering decomposition, or dissociation, in its conversion into vapor.

Two essentially different principles underlie the methods employed in determining the vapor density. According to one, by weighing a vessel of known capacity filled with vapor, we ascertain the weight of the latter—method of Dumas and Bunsen. Or, in accordance with the other principle, a weighed quantity of substance is vaporized and the volume of the resulting vapor determined. In this case the vapor volume may be directly measured—methods of Gay-Lussac and A. W. Hofmann ; or it may be calculated from the equivalent quantity of a liquid expelled by the vapor—displacement methods. The first three methods, of which a fuller description may be found in more extended text-books,* are seldom employed at present in laboratories, because the recently published method of V. Meyer, characterized by sim-

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* Consult Handwörterbuch der Chemie, Ladenburg, Bd. 3, 244.

plicity in execution, affords sufficiently accurate results for all ordinary purposes.

Method of Victor Meyer.—Vapor density determination by *air displacement.** According to this a weighed quantity of substance is vaporized in an enclosed space, when it displaces an equal volume of air, which is measured. Fig. 2 represents the apparatus constructed for this purpose. It consists of a narrow glass tube, to which is fused the cylindrical vessel, *A*. The upper, somewhat enlarged opening, *B*, is closed with a caoutchouc stopper. There is also a short capillary gas-delivery tube, *C*, intended to conduct out the displaced air. It terminates in the water bath, *D*. The substance is weighed out in a small glass tube provided with a stopper, and vaporized in *A*. The escaping air is collected in the eudiometer, *E*. The vapor-bath, used in heating, consists of a wide glass cylinder, *F*,† whose lower, somewhat enlarged end, is closed and filled with a liquid of known boiling point. The liquid employed is determined by the substance under examination; its boiling point must be above that of the latter. Some of the liquids in use are water (100°), xylene (about 140°), aniline (184°), ethyl benzoate (213°), amyl benzoate (261°), and diphenylamine (310°).

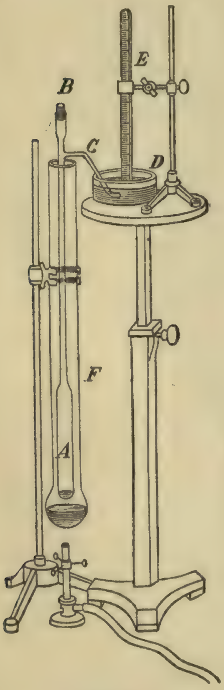

FIG. 2.

The vapor density, S, equals the weight of the vapor, P (afforded by the weight of the substance employed), divided by the weight of an equal volume of air, P′—

$$S = \frac{P}{P'}.$$

1 c.cm. of air at 0° and 760 mm. pressure weighs 0.001293 gram. The air volume V_t, found at the observed temperature is under the pressure $p - s$, in which p indicates the barometric pressure and s the tension of the aqueous vapor at temperature t. The weight then would be—

$$P' = 0.001293. \quad V_t. \quad \frac{1}{1 + 0.00367\,t}.\frac{p - s}{760}.‡$$

Consequently the vapor density sought is—

$$S = \frac{P\ (1 + 0.00367\ t.)\ 760}{0.001293.\quad V_t\ (p - s)}$$

The displaced air may be collected in the *gasbaroscope* (compare p. 22). (B. 27, 2267.)

V. Meyer's method yields results that are perfectly satisfactory *practically*, although not without some slight error in principle. However, they answer, because in deducing the molecular weight from the vapor density, relatively large numbers are considered and the little differences discarded. A greater inaccuracy may arise in the method in filling in the substances as described, because air is apt to enter the vessel. L. Meyer (B. 13, 991), Piccard, (*ibid.* 13, 1080), Mahlmann (*ibid.* 18, 1624), and V. Meyer and Biltz (*ibid.* 21, 688) have suggested different devices to avoid this source of error. To test the decomposability of the

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* B. 11, 1867, 2253.

† B. 19, 1862.

‡ It is simpler to make the reduction to 760 mm. and 0° by comparison with a normal volume (p. 22).

substance at the temperature of the experiment, heat a small portion of it in a glass bulb provided with a long point (B. **14**, 1466).

Substances boiling above 300° are heated in a lead-bath (B. **11**, 2255). Porcelain vessels are used when the temperature required is so high as to melt glass, and the heating is conducted in gas ovens (B. **12**, 1112). Where air affects the substances in vapor form, the apparatus is filled with pure nitrogen. (Compare B. **18**, 2809; **21**, 688.) When the substances under investigation attack the porcelain, tubes of platinum are substituted for the latter. These are enclosed in glazed porcelain tubes, and heated in furnaces (B. **12**, 2204; Z. phys. Ch. **1**, 146; B. **21**, 688). This form of apparatus allows of the simultaneous determination of temperature (B. **15**, 141; Z. phys. Ch. **1**, 153).

For modifications in methods of determining the density of gases, consult V. Meyer, B. **15**, 137, 1161 and 2771; Langer and V. Meyer, Pyrotechnische Untersuchungen, 1885; Crafts, B. **13**, 851, **14**, 356, and **16**, 457. For air-baths and regulators see L. Meyer, B. **16**, 1087; **17**, 478.

Modifications of the displacement method, adapted for work under reduced pressure, have been proposed by La Coste (B. **18**, 2122), Schall (B., **22**, 140; B. **27**, R. 604), Eyckmann (B. **22**, 2754), V. Meyer and Demuth (B. **23**, 311; Richards (B. **23**, 919, note), Neuberg (B. **24**, 729, 2543).

For the method of Nilson and Pettersson, see B. **17**, 987 and **19**, R. 88; also J. pr. Ch. **33**, **1**. See B. **21**, 2767, for the method of Biltz.

(3) *Determination of the Molecular Weight of Substances when in Solution.*

1. **By Means of Osmotic Pressure.**—Recently van 't Hoff (Z. phys. Ch. **1**, 481; **3**, 198; B. **27**, 6) has developed an exceedingly important theory in regard to solutions.* According to this new idea chemical substances, when in dilute solution, exhibit a deportment similar to that observed when in a gaseous or vapor-form; therefore, the laws applicable to gases (Boyle, Gay-Lussac, and Avogadro) possess the same value for solutions. We know that the gas-particles exert pressure, and it is also true that the particles of compounds, when dissolved, exert a pressure, which is directly expressed or shown by the osmotic phenomena, and hence it is termed *osmotic pressure*. This pressure is equal to that which would be exerted by an equal amount of the substance, if it were converted into gas, and occupied the same volume, at the same temperature, as the solution. Solutions containing molecular quantities of different substances exert the same osmotic pressure. It is, therefore, possible, as in the case of gas-pressure, to directly deduce the molecular weight of the substances in solution from this osmotic pressure.

Pfeffer determines osmotic pressure by means of artificial cells, having semipermeable walls. If suitably modified this method promises to be of wide applicability (Ladenburg, B. **22**, 1225).

The *plasmolytic method* of de Vries (Z. phys. Ch. **2**, 415), employed in determining osmotic pressure, is based upon the use of living plant cells.

To calculate the molecular weight, make use of the general formula for gases: $pv = RT$, in which R represents a constant, and T the absolute temperature, calcu-

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* See Ostwald's Grundriss der allgemeinen Chemie, 2. Aufl. 1890; Lothar Meyer, Grundzüge der theoretischen Chemie, 2. Aufl. 1893.

lated from — 273° forward. If this equation is also to include the law of Avogadro (that the molecular weights of gases or dissolved substances occupy the same volume at like temperature and pressure), then molecular quantities of the substances must always be taken into consideration. The constant equals 84500 for gram molecular weights (2 grams hydrogen, or 31.92 grams oxygen) at the temperature 0° (or 273°), and the pressure (gas or osmotic pressure) of 76 cm. of mercury.

$$p \,.\, v = 84500 \,.\, T.^*$$

v represents the volume corresponding to the gram molecular weight ($v = \frac{M}{a}$, in which a is the weight in grams of 1 c.cm. of the gas, or dissolved substance, contained in 1 c.cm. of the solution). Substituting figures the formula would read: $p \,.\, 13.59 \times \frac{M}{a} = 84500\ (273 + t)$, with the four variables p, M, a and t. If three of these be given the fourth can be calculated. Consequently, the molecular weight M is found from the formula:—

$$M = \frac{a \,.\, 84500\,(273 + t)}{p \,.\, 13.59} = \frac{a \,.\, 6218\,(273 + t)}{p}.$$

2. **From the Lowering of the Vapor Pressure or the Elevation of the Boiling Point.**—The lowering of the vapor pressure of solutions is closely allied to osmotic pressure. It is a known fact that solutions at the same temperature have a lower vapor pressure (f') than the pure solvent (f), and consequently boil at a more elevated temperature than the latter. The lowering in pressure ($f - f'$) is in proportion to the quantity of the substance dissolved (Wüllner). This harmonizes with the equation $\frac{f - f'}{f} = k\,g$, in which k represents the "relative lowering of the vapor pressure" $\left(\frac{f - f'}{f}\right)$ for 1 per cent. solutions, and g their percentage content.

If the lowering be referred not to equal quantities, but rather to molecular quantities of the substances dissolved, it will be discovered that equi-molecular solutions (those containing molecular quantities of the different substances in equal amounts in the same solvent) show equal lowering—the molecular vapor pressure lowering is constant:—

$$M \,.\, \frac{f - f'}{f} = C.$$

Again, on comparing the relative lowering of vapor pressure in different solvents, it will be found also that they are equal, if equal amounts of the substances are dissolved in molecular quantities of the solvent. In its broadest sense the law would read: The lowering of vapor-pressure is to the vapor-pressure of the solvent (f) as the number of molecules of the dissolved body (n) is to the total number of molecules (n + N):—

$$\frac{f - f'}{f} = \frac{n}{n + N}.$$

Substituting the quotients $\frac{g}{m}$ and $\frac{G}{M}$ (g and G represent the weight quantities

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* $R = \frac{p\,v}{T}$; $p = 1033 = 76 \times 13.59$ (sp. gr. of mercury); $v = 22330 = 32.92/0.001430$ (wt. of 1 c.cm. of oxygen). $R = \frac{1033 \times 22330}{273}$.

of the substance and the solvent; m and M are their molecular weights), for n and N, it will be easy to calculate the molecular weights.

F. M. Raoult (1887) developed these rules empirically. Soon thereafter van 't Hoff (Z. phys. Ch. **3**, 115) deduced them theoretically from the osmotic pressure. They are only of value for non-volatile (as compared with the solvent) substances, or such as volatilize with difficulty. The same abnormalities observed with osmotic pressure and depression in the freezing point also appear here.

The methods for the determination of vapor-pressure are yet too little known and primitive in their nature to be applied in the practical determination of molecular weights (B. **22**, 1084; Z. phys. Ch. **4**, 538). It is easier to determine the rise in the boiling points; this is also more reliable (Beckmann, Z. phys. Ch. **4**, 539; **6**, 437; **8**, 223; **15**, 656; B. **27**, R. 727; **28**, R. 432).

Method of Beckmann.—A small flask (Fig. 3) provided with three tubulures is used as the boiling vessel. A platinum wire s is fused into its bottom. This accelerates the boiling. The flask is filled one-half (f) with glass beads. The wide side-tube D supports an accurate thermometer (Walferdin), which reaches to the contents of the vessel. Later its mercury reservoir is wholly immersed in the solvent. The condenser B is fixed in b, so that the vapors can only reach it through the opening d. Its lower end should terminate about 1 cm. above the glass pearls, in order that rising vapor-bubbles do not retard the returning liquid. The flask, closed with stoppers, is carefully weighed to centigrams, and the solvent introduced until its level is at e. Its quantity is found by reweighing. The boiling vessel is now surrounded by an asbestos mantle, filled out above with cotton, but with an exposed bottom. The return-tube B is connected with a Soxhlet bulb-cooler or, if the metal is attacked, with an ordinary Liebig condenser. Note the boiling point of the solvent, and after the introduction of the substance through the tube C, determine the boiling point a second time. In this way we ascertain the rise in boiling point. Beckmann has so modified this apparatus as to make it applicable to solvents having high boiling points (Z. phys. Ch. **8**, 223). S. Arrhenius has deduced a formula for molecular rise in boiling point, which is perfectly analogous to that deduced by van 't Hoff for the molecular depression of the freezing point. The molecular rise d is: $d = 0.02.\frac{T^2}{w}$, in which T represents the absolute boiling point, and w the heat of evaporation of the solvent. Upon dissolving 1 gram-molecule of a substance, *i. e.*, if the molecular weight of the body is m, with m g of it in 100 grams of solvent, the boiling point will be raised about d°, upon dissolving pg of the substance in 100 gr. of solvent about $d_1 = d.\frac{p}{m}$; from which

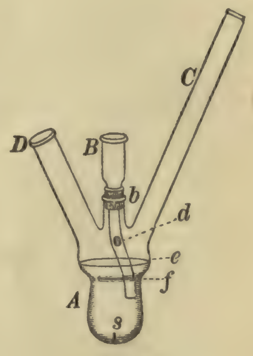

FIG. 3.

$$m = p.\frac{d}{d_1}.$$

In this equation

p = the weight (in grams) of the substance, dissolved in 100 grams of the solvent,

d = molecular rise in boiling point $\left(= 0.02.\frac{T^2}{w}\right)$,

d_1 = observed rise in boiling point.

The molecular elevation of the boiling point in the case of ether is 21.1°, of chloroform 36.6°, and of acetic acid 25.3°.

A. Naumann, B. **11**, 429, has devised a method for molecular weight determination by the distillation of liquids not miscible with water. He conducts steam through them.

3. **From the Depression of the Freezing Point.**—The molecular weights of dissolved substances are more accurately and readily deduced from the depression of the freezing points of their solutions. Blagden in 1788, and Rüdorff in 1861, found that the depression of the freezing points of crystallizable solvents, or substances (as water, benzene and glacial acetic acid) is proportional to the quantity of substance dissolved by them. The later researches of Coppet (1871), and especially those of Raoult (1882), have established the fact that when molecular quantities of different substances are dissolved in the same amount of a solvent they show the same depression in their freezing points (Law of Raoult). If t represents the depression produced by p grams of substance in 100 grams of the solvent, the co-efficient of depression $\frac{t}{p}$ will be the depression for 1 gram of substance in 100 grams of the solution.* The *molecular depression* is the product obtained by multiplying the depression co-efficient and the molecular weight of the dissolved substances. This is a constant for all substances having the same solvent:—

$$M \,.\, \frac{t}{p} = C.$$

Raoult's experiments show the constant to have the following values: for benzene 49; for glacial acetic acid 39; for water 19. When the constant is known the molecular weight is calculated as follows:—

$$M = C\,\frac{p}{t}.$$

A comparison of the constants found for different solvents will disclose the fact that they bear the same ratio to each other as the molecular weights—that consequently the quotient obtained from the molecular depressions and molecular weights is a constant value (about 0.62). It means, expressed differently, that the molecule of any one substance dissolved in 100 molecules of a liquid lowers the point of solidification very nearly 0.62.

Guldberg (1870) and van 't Hoff (1886) have since made a theoretical deduction of these laws from the lowering of the vapor pressure, and from the osmotic pressure. The constant C is obtained, for the various solvents, from the formula $0.02\,\frac{T^2}{w}$. Here T indicates the temperature of solidification of the solvent calculated from the absolute zero-point forward; w is its latent heat of fusion. In this way van 't Hoff calculated the constants for benzene (53), acetic acid (38.8), and water 18.9 (see above).

The laws just described possess a direct value for indifferent substances, having but slight chemical activity. Salts, strong acids and

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* Arrhenius (Z. phys. Ch. **2**, 493) expresses the content of solutions by the weight in grams of the substances contained in 100 c.c. of the solution.

bases (all electrolytes) constitute the exceptions. The depressions in freezing point are greater for these than their calculated values (they also have greater osmotic pressure, and greater lowering of the vapor pressure). The electrolytic dissociation theory of Arrhenius (Z. phys. Ch. **1**, 631, 577; **2**, 491; B. **27**, R. 542) would account for this by the assumption that the electrolytes have separated into their free ions. However even the indifferent bodies exhibit many abnormalities—generally the very opposite of the ordinary. These seem to be due to the fact that the substances held in solution had not completely broken up into their individual molecules. The most accurate results are obtained by operating with very dilute solutions, and by employing glacial acetic acid as solvent. This dissociates solids most readily.

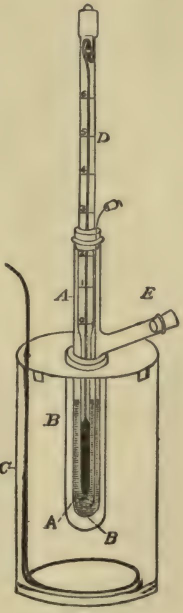

FIG. 4.

FIG. 5.

Various forms of apparatus suitable for the above purpose, and methods of working have been proposed by Auwers,[*] Hollemann (B. **21**, 860), Hentschel,[†] Beckmann,[‡] Eykmann,[§] Klobukow,[‖] and Baumann and Fromm (B. **24**, 1431).

Beckmann's Method.—A hard glass tube, *A*, 2–3 cm. in width, side projection *E* (Fig. 4), is filled with 15–20 grams of the solvent (weighed out accurately in centigrams), and closed with a stopper, in which are placed an accurate thermometer (Walferdin), and a stout platinum wire serving as a stirring rod. The lower part of the tube is attached by means of a cork to a somewhat larger, wider tube. The latter serves as an air-jacket. The entire apparatus projects into a beaker glass filled with a freezing mixture. Cold water will answer for glacial acetic acid (congealing at 16°), and ice-water for benzene (about 5°). First determine the congealing point of the solvent by cooling it 1–2° below its freezing point, and then by agitation with the platinum rod (after addition of platinum clippings), induce the formation of crystals. During this operation the thermometer rises, and when the mercury is stationary it indicates the freezing point of the solvent. Allow the mass to melt, and introduce an accurately weighed amount of substance through *E*. When this has dissolved the freezing point is re-determined as before (B. **28**, R. 412).

Eykmann's Method.—(A. **273**, 98). By this method it is possible to use smaller amounts of solution (6–8 grams) and substance. This is done by using phenol (m. p. about 38°), as the solvent. Its molecular depression has been theoretically deduced; it is about 76 (see above). Fig. 5 represents the form of appa-

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[*] B. **21**, 711; [†] Z. phys. Ch. **2**, 307; [‡] *Ibid.* **2**, 638; [§] *Ibid.* **2**, 964; [‖] *Ibid.* **4**, 10.

ratus proposed by Eykmann. It is nothing more than a flask with two tubulures, in one of which a thermometer is fixed, and over the other is placed a ground-glass cap.

Paterno's investigations show, contrary to earlier observations, that when benzene is employed as the solvent the carbon derivatives mostly yield normal results; the exceptions being the alcohols, phenols, acids, oximes and pyrrol (B. **22**, 1430 and Z. phys. Ch. **5**, 94; B. **27**, R. 845; **28**, R. 974).

Naphthalene may also be used for determinations of this kind. van 't Hoff gives its depression constant as equal to about 70 (B. **22**, 2501; **23**, R. **1**; **24**, 1431).

Consult B. **28**, 804 for a method of determining molecular weights from the decrease in solubility.

For the determination of molecular weight from molecular solution-volume see B. **29**, 1023.

THE CHEMICAL CONSTITUTION OF THE CARBON COMPOUNDS.

Early Theories.—The opinion that the cause of chemical affinity resided in electrical forces, came to light in the commencement of this century, when the remarkable decompositions of chemical bodies, through the agency of the electric current, were discovered. It was assumed that the elementary atoms possessed different electrical polarities, and the elements were arranged in a series according to their electrical deportment. Chemical union depended on the obliteration of different electricities. The *dualistic* idea of the constitution of compounds was a necessary consequence of this hypothesis. According to it, every chemical compound was composed of two groups, electrically different, and these were further made up of two different groups or elements. Thus, salts were viewed as combinations of electro-positive bases (metallic oxides), with electro-negative acids (acid anhydrides), and these, in turn, were held to be binary compounds of oxygen with metals and non-metals. With this basis, there was constructed the *electro-chemical, dualistic theory of Berzelius.* This prevailed almost exclusively in Germany until about 1860.

The principles predominating in inorganic chemistry were also applied to organic substances. It was thought that in the latter complex groups (radicals) pre-existed, and played the same rôle that the elements did in mineral matter. Organic chemistry was defined as the chemistry of the compound radicals (Liebig, 1832), and led to the *chemical-radical theory*, which flourished in Germany simultaneously with the *electro-chemical* theory. According to this view, the object of organic chemistry was the investigation and isolation of radicals, in the sense of the dualistic idea, as the more intimate components of the organic compounds, and by this means they sought to explain the constitution of the latter. (Liebig and Wöhler, Ueber das Radical der Benzoësäure, A. **3**, 249; Bunsen, Ueber die Kakodylverbindungen, A. **31**, 175; **37**, 1; **42**, 14; **46**, 1.)

In the meantime, about 1830, France contributed facts not in harmony with the electro-chemical, dualistic theory. It had been found that the hydrogen in organic compounds, could be replaced (substituted) by chlorine and bromine, without any apparent change in the character of the compounds. To the electro-negative halogens was ascribed a chemical function similar to electro-positive hydrogen. This showed the electro-chemical hypothesis to be erroneous. The dualistic idea was superseded by a *unitary* theory. Laying aside all the primitive speculations on the nature of chemical affinity, the chemical compounds began to be looked upon as constituted in accordance with definite mechanical ground-forms—*types*—in which the individual elements could be replaced by others (early type theory of Dumas, nucleus theory of Laurent). Dumas, however, distinguished between *chemical* types and *mechanical* types. He considered substances to have the same *chemical* type, to be of the same species, when they possessed like fundamental properties, *e. g.*, acetic and chloracetic acids. Like Regnault he said they were of the same mechanical type, belonged to the same natural family, when they were related in structure but manifested a different chemical character: alcohol and acetic acid. At the same time the dualistic view on the pre-existence of radicals was refuted.

The correct establishment of the ideas, *equivalent*, *atom and molecule* (Laurent and Gerhardt), was an important consequence of the typical unitary idea of chemical compounds. By means of it a correct foundation was laid for further generalization. The molecule having been determined a chemical unit, the study of the grouping of atoms in the molecule became possible, and chemical constitution could again be more closely examined. The investigation of the reactions of double decomposition, whereby single atomic groups (radicals or residues) were preserved and could be exchanged (Gerhardt); the important discoveries of the amines or substituted ammonias by Würtz (1849), and Hofmann (1849); the epoch-making researches of Williamson and Chancel (1850), upon the composition of ethers, and the discovery of acid-forming oxides by Gerhardt (1851)—led to a "type" explanation of the individual classes of compounds. Williamson referred the alcohols and ethers to the water type. A. W. Hofmann deduced the substituted ammonias from ammonia. The "type" idea found its culmination in the *type theory of Gerhardt* (1853), which was nothing more than an amalgamation of the early type or substitution theory of Dumas and Laurent with the radical theory of Berzelius and Liebig. The molecule was its basis—and to it there was attached a more extended grouping of the atoms in the molecule. The conception of radicals became different. They were no longer regarded as atomic groups that could be isolated and compared with elements, but as molecular residues which remained unaltered in certain reactions.

Comparing the carbon compounds with the simplest inorganic derivatives, Gerhardt referred them to the following principal fundamental forms or types:—

$\left.\begin{matrix}H\\H\end{matrix}\right\}$	$\left.\begin{matrix}Cl\\H\end{matrix}\right\}$	$\left.\begin{matrix}H\\H\end{matrix}\right\}O$	$\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N$
Hydrogen.	**Hydrogen Chloride.**	**Water.**	**Ammonia.**

From these they could be obtained by substituting the compound radicals for hydrogen atoms. All compounds that could be viewed as consisting of two directly combined groups were referred to the hydrogen and hydrogen chloride types, *e. g.*:—

$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}$	$\left.\begin{matrix}C_2H_5\\Cl\end{matrix}\right\}$	$\left.\begin{matrix}CN\\H\end{matrix}\right\}$	$\left.\begin{matrix}C_2H_5\\CN\end{matrix}\right\}$	$\left.\begin{matrix}C_2H_3O\\Cl\end{matrix}\right\}$
Ethyl Hydride.	**Ethyl Chloride.**	**Cyanogen Hydride.**	**Ethyl Cyanide.**	**Acetyl Chloride.**

It is customary to refer all those bodies derivable from water by the replacement of hydrogen, to the water type:—

$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O$	$\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O,$	$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O$	$\left.\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right\}O$
Alcohol.	**Acetic Acid.**	**Ethyl Ether.**	**Acetic Anhydride.**

Associated types were included with the principal types. Thus, with the fundamental type $\left.\begin{matrix}Cl\\H\end{matrix}\right\}$ were arranged as subordinates, the types $\left.\begin{matrix}Br\\H\end{matrix}\right\}$ $\left.\begin{matrix}I\\H\end{matrix}\right\}$; with the water type $\left.\begin{matrix}H\\H\end{matrix}\right\}O$ that of $\left.\begin{matrix}H\\H\end{matrix}\right\}S$, etc.

The compounds containing three groups united by nitrogen are considered ammonia derivatives:—

$$\left.\begin{matrix}CH_3\\H\\H\end{matrix}\right\}N \qquad \left.\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\right\}N \qquad \left.\begin{matrix}C_2H_3O\\H\\H\end{matrix}\right\}N \qquad \left.\begin{matrix}CO\\H\end{matrix}\right\}N$$

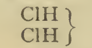
The types of Gerhardt were chemical types. He thus expressed himself: "Mes types sont des types de double décomposition." It is thus understood that he included the type $\left.\begin{matrix}H\\Cl\end{matrix}\right\}$ with that of $\left.\begin{matrix}H\\H\end{matrix}\right\}$.

These types no longer possessed their early restricted meaning. Sometimes a compound was referred to different types, according to the transpositions the formula was intended to express. Thus aldehyde was referred to the hydrogen or water type ; cyanic acid to the water or ammonia type :—

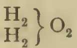
$$\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\} \quad \text{and} \quad \left.\begin{matrix}C_2H_3\\H\end{matrix}\right\}O, \qquad \left.\begin{matrix}CN\\H\end{matrix}\right\}O \quad \text{and} \quad \left.\begin{matrix}CO\\H\end{matrix}\right\}N$$

The development of the idea of polyatomic radicals, the knowledge that the hydrogen of carbon radicals could be replaced by the groups OH and NH_2, etc., contributed to the further establishment of *multiple* and *mixed types* (Williamson, Odling, Kekulé) :—

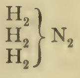
Compound Types :—



$$\left.\begin{matrix}ClH\\ClH\end{matrix}\right\}$$

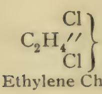


$$\left.\begin{matrix}H_2\\H_2\end{matrix}\right\}O_2$$



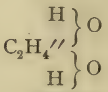
$$\left.\begin{matrix}H_2\\H_2\\H_2\end{matrix}\right\}N_2$$

e. g.:—



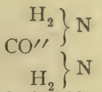
$$\left.\begin{matrix}Cl\\C_2H_4''\\Cl\end{matrix}\right\}$$

Ethylene Chloride.



$$\begin{matrix}\left.\begin{matrix}H\\C_2H_4''\end{matrix}\right\}O\\\left.\begin{matrix}\\H\end{matrix}\right\}O\end{matrix}$$

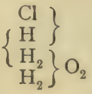
Ethylene Glycol.



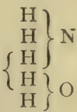
$$\begin{matrix}\left.\begin{matrix}H_2\\CO''\end{matrix}\right\}N\\\left.\begin{matrix}\\H_2\end{matrix}\right\}N\end{matrix}$$

Carbamide.

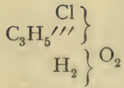
Mixed Types :—



$$\begin{matrix}\left.\begin{matrix}Cl\\H\end{matrix}\right\}\\\left.\begin{matrix}H_2\\H_2\end{matrix}\right\}O_2\end{matrix}$$

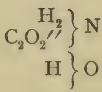


$$\begin{matrix}\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N\\\left.\begin{matrix}H\\H\end{matrix}\right\}O\end{matrix}$$



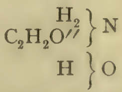
$$\begin{matrix}\left.\begin{matrix}Cl\\C_3H_5'''\end{matrix}\right\}\\\left.\begin{matrix}H_2\end{matrix}\right\}O_2\end{matrix}$$

Chlorhydrin.



$$\begin{matrix}\left.\begin{matrix}H_2\\C_2O_2''\end{matrix}\right\}N\\\left.\begin{matrix}H\end{matrix}\right\}O\end{matrix}$$

Oxamic Acid.

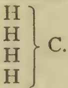


$$\begin{matrix}\left.\begin{matrix}H_2\\C_2H_2O''\end{matrix}\right\}N\\\left.\begin{matrix}H\end{matrix}\right\}O\end{matrix}$$

Amido-acetic Acid.

The manner of arrangement finding expression in these multiple and mixed types was this: two or more groups were united into one whole—a molecule—by the univalent radicals. Upon comparing these typical with the structural formulas employed at present, we observe that the first constitute the transitional state from the empiric, unitary formulas to those of the present day. The latter aim to express the perfect grouping of the atoms in the molecule.

The next step was the expansion of the Gerhardt type to the type of—



marsh-gas $\left.\begin{matrix}H\\H\\H\\H\end{matrix}\right\}C$. This was the work of Kekulé, 1856 (A. 101, 204).

Recent Views.—Kekulé (1857) in a communication, Ueber die sog. gepaarten Verbindungen und die Theorie der mehratomigen Radicale (A. 104, 129) indicated the idea of types by the assumption of a peculiar function of the atoms—their atomicity or basicity (valence). This he supposed to be the cause of the types of Gerhardt. As early as 1852 Frankland enunciated similar views in regard to the elements of the nitrogen group (A. **25**, 329; **101**, 257; Frankland: Experimental Researches in Pure, Applied and Physical Chemistry, London, 1871, p. 147). Kolbe concurred with these ideas (compare his derivation of the organic compounds from the radical carbonyl C_2 and carbon dioxide C_2O_4—Kolbe's Lehrbuch der organischen Chemie, 1858, Bd. I, p. 567). The reason that they did not exert greater influence upon the development of theoretical chemistry is mainly due to the fact that the notions of the relations of equivalent weight and atomic weight were not clearly defined by Kolbe and Frankland.

In his assumptions Kekulé rather returned to Dumas' mechanical types, than to the double decomposition types of Gerhardt. The distinction between the type $\left.\begin{matrix}H\\H\end{matrix}\right\}$ and $\left.\begin{matrix}Cl\\H\end{matrix}\right\}$ as drawn by Gerhardt did not exist for Kekulé. The latter in 1858 said, "it is necessary in explaining the properties of chemical compounds to go back to the elements which compose these compounds." He continues: "I do not regard it as the chief aim of our time to detect atomic groups which, owing to certain properties, may be considered radicals and thus to include the compounds under certain types, which in this way have scarcely any other significance than that of type or example formula. I am rather of the opinion that the generalization should be extended to the constitution of the radicals themselves, to the determination of the relation of the elements among themselves, and thus to deduce from the nature of the elements both the nature of the radicals and that of their compounds." (A. **106**, 136.)

The recognition of the quadrivalence of the carbon atoms and the power they possessed of combining with each other, accounted for the existence and the combining value of radicals; also, for their constitution (Kekulé, *l. c.*, and Couper, A. ch. phys. [3] **53**, 469). The type theory, consequently, is not as sometimes declared, laid aside as erroneous; it has only found generalization and amplification in a broader principle: the extension of the valence theory of Kekulé and Couper to the derivatives of carbon.

While formerly it was customary to consider in addition to *empiric* formulas, representing merely an atomic composition of the molecule, *rational* formulas (Berzelius), which in reality were nothing more than rearrangement formulas adopted to explain to a certain degree the chemical behavior of derivatives of carbon, Kekulé spoke of the *manner of union of the atoms in the molecule*, by knowledge of which the constitution of the carbon compounds is determined (constitution formulas). Lothar Meyer next introduced the phrase "*linking of the carbon atoms*." The expression *structure* (structural formulas) originated with Butlerow.

An application of the valence theory, which has been remarkably fruitful, is the Kekulé benzene theory. Here for the first time there was assumed present in a carbon compound a closed carbon-chain, a ring consisting of six carbon atoms. The rather singular stability of the aromatic bodies is due to the presence of this "benzene ring." Körner applied these views to pyridine and deduced the pyridine ring. In rapid succession numerous other rings have followed and have arranged themselves side by side with the old rings in more recent years.

Theory of Chemical Structure of Carbon Compounds. Theory of Atomic Linking or the Structural Theory.

Constitutional or structural formulas are based upon the following principles, which have been deduced from experiment and repeatedly confirmed by the same.

1. *The carbon atom is quadrivalent* The position of carbon in the periodic system gives expression to this fact. One carbon atom can combine at the most with four dissimilar or similar univalent atoms or atomic groups:

CH_4	CF_4	CCl_4
Methane.	Carbon Tetrafluoride.	Carbon Tetrachloride.

CH_3Cl	CH_3NH_2	CH_2Cl_2	$CHCl_3$
Methyl Chloride.	Methylamine.	Dichlormethane.	Chloroform.

In a few compounds, *e. g.*, carbon monoxide CO and the isonitriles or carbylamines $R'-N=C$ (A. 270, 267) and fulminic acid $HO-N=C$ (A. 280, 303) carbon figures as a bivalent element.

2. *The four affinity units of carbon are, as generally represented, equal and similar, i. e.*, no differences can be discovered in them when they form compounds.

If one of the four hydrogen atoms in the simplest hydrocarbon, CH_4, be replaced by a univalent atom or univalent atomic group, each monosubstitution product will appear in but one modification. The four hydrogen atoms are similarly combined, consequently it is immaterial which of them is replaced.

CH_3Cl	CH_3OH	CH_3NH_2
Chlormethane.	Methyl Alcohol.	Methylamine.

are known in but one modification each (p. 46).

3. *The carbon atoms can unite* with each other. When two carbon atoms combine the union can occur in three ways:

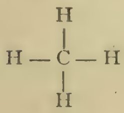
(*a*) The two carbon atoms unite with a single valence each, leaving the atomic group, $\equiv C-C\equiv$, with six free valences.

(*b*) The two carbon atoms unite with two valences each, then the atomic group, $=C=C=$, with four free valences, remains.

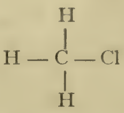
(*c*) Two carbon atoms are united by three valences. The residual group $-C\equiv C-$ has but two uncombined valences.

In the first case the union of the two carbon atoms is *single*, in the second case *double*, and in the third case *triple*. Carbon atoms can combine to a greater degree with themselves than the atoms of any other elements. This gives rise to carbon nuclei, carbon skeletons, which form either open or closed carbon chains or rings. The uncombined valences of the carbon nuclei can saturate or take up the atoms of other elements or other atomic groups. This would explain the existence of the almost numberless carbon compounds.

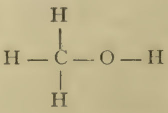
The mutual union is indicated by formulas or, according to the recommendation of Couper, by lines. These formulas represent the structure of the compounds; they are structural formulas:



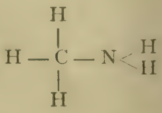
$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ H & - & C & - & H \\ & & | & & \\ & & H & & \end{array}$$



$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ H & - & C & - & Cl \\ & & | & & \\ & & H & & \end{array}$$

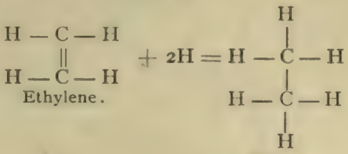


$$\begin{array}{ccccccc} & & H & & & & \\ & & | & & & & \\ H & - & C & - & O & - & H \\ & & | & & & & \\ & & H & & & & \end{array}$$



$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ H & - & C & - & N<\begin{smallmatrix}H\\H\end{smallmatrix} \\ & & | & & \\ & & H & & \end{array}$$

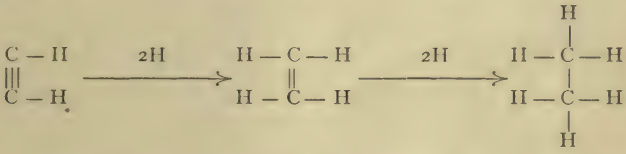
Saturated and Unsaturated Compounds.—Saturated carbon compounds are those in which the carbon atoms are united by a single bond to each other. They cannot be united by more valences unless the carbon chain is broken up. Unsaturated compounds are those in which a double or triple union between carbon atoms exists. As a single union is sufficient to link carbon atoms together, a pair of carbon atoms with double union can take up two additional valence units. This would dissolve the double union, giving rise to single linkage without destruction of the chain, *e. g.*



$$\begin{array}{c} H-C-H \\ \Vert \\ H-C-H \end{array} + 2H = \begin{array}{c} H \\ | \\ H-C-H \\ | \\ H-C-H \\ | \\ H \end{array}$$

Ethylene. Ethane.

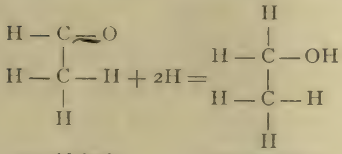
Two carbon atoms, trebly linked, can take up four valences. The dissolution of the triple union may proceed step by step. The triple linkage may first be changed to a double linkage and then to a simple union :—



$$\begin{array}{l} C-H \\ ||| \\ C-H \end{array} \xrightarrow{2H} \begin{array}{c} H-C-H \\ \Vert \\ H-C-H \end{array} \xrightarrow{2H} \begin{array}{c} H \\ | \\ H-C-H \\ | \\ H-C-H \\ | \\ H \end{array}$$

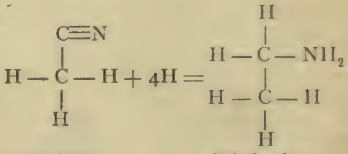
The unsaturated compounds, by the breaking-down of their double and triple unions and the addition of two or four univalent atoms, pass into saturated compounds.

This same deportment is observed with many other compounds containing carbon and oxygen, doubly combined, $=C=O$ (aldehydes and ketones) or double and triple union of carbon and nitrogen, $=C=N-C\equiv N$ (acid nitriles, imides, oximes). They are in the same sense unsaturated; by the breaking down of their double or triple union they change to saturated compounds in which the polyvalent atoms are linked by a single bond to each other:



$$\begin{array}{c} H-C=O \\ | \\ H-C-H \\ | \\ H \end{array} + 2H = \begin{array}{c} H \\ | \\ H-C-OH \\ | \\ H-C-H \\ | \\ H \end{array}$$

Acetaldehyde. Ethyl Alcohol.



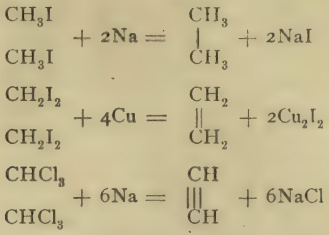
$$\begin{array}{c} C\equiv N \\ | \\ H-C-H \\ | \\ H \end{array} + 4H = \begin{array}{c} H \\ | \\ H-C-NH_2 \\ | \\ H-C-H \\ | \\ H \end{array}$$

Acetonitrile. Ethylamine.

Radicals, Residues, Groups.—The assumption of radicals, able to exist alone and play a special rôle in molecules, has been abandoned. The structural formulas are unitary formulas—they give no especially favorable position to one atom over another in the molecule. Radicals are atomic groups, chiefly those containing carbon, which in many reactions are unaltered and pass from one compound into another. In this category must also be included the uni-, bi-, tri-, and polyvalent atomic complexes, which remain when atoms or atomic groups are removed from saturated bodies. By the gradual removal of hydrogen methane yields the following radicals, having different valences:

CH_4	$-CH_3$	$=CH_2$	$\equiv CH$
Methane saturated.	**Methyl univalent radical.**	**Methylene bivalent radical.**	**Methenyl or Methine trivalent radical.**

If such radicals are isolated from proper compounds, *e. g.*, the halogen derivatives, then two of them unite to form a molecule:

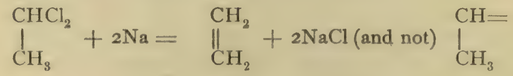


$$\begin{array}{l} CH_3I \\ CH_3I \end{array} + 2Na = \begin{array}{c} CH_3 \\ | \\ CH_3 \end{array} + 2NaI$$

$$\begin{array}{l} CH_2I_2 \\ CH_2I_2 \end{array} + 4Cu = \begin{array}{c} CH_2 \\ \| \\ CH_2 \end{array} + 2Cu_2I_2$$

$$\begin{array}{l} CHCl_3 \\ CHCl_3 \end{array} + 6Na = \begin{array}{c} CH \\ ||| \\ CH \end{array} + 6NaCl$$

Or, an atomic rearrangement may occur with the production of a molecule of the same number of carbon atoms:



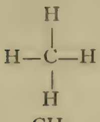
$$\begin{array}{l} CHCl_2 \\ | \\ CH_3 \end{array} + 2Na = \begin{array}{l} CH_2 \\ \| \\ CH_2 \end{array} + 2NaCl \text{ (and not) } \begin{array}{l} CH= \\ | \\ CH_3 \end{array}$$

The expressions *residue* and *group* are similar to *radical*. They are chiefly applied to inorganic radicals, *e. g.*,

$-OH$	water residue or hydroxyl group,
$-SH$	hydrogen sulphide residue or sulphydrate group,
$-NH_2$	ammonia residue or amido group,
$=NH$	imido group,
$-NO_2$	nitro group,
$-NO$	nitroso group.

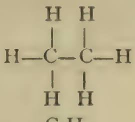
Homologous and Isologous Series.—Schiel, in 1842 (A. 43, 107; 110, 141), directed attention to the phenomenon of homology, giving as evidence the alcohol radicals. Shortly after Dumas observed it in the fatty acids. Gerhardt introduced the terms *homologous* and *isologous series*, and showed the rôle these series assumed in the classification of the carbon derivatives. It was the theory of atomic linking that first disclosed the cause of homology.

The different manner, in the linking of the carbon atoms, shows itself most plainly in their hydrogen compounds—in the so-called hydrocarbons. By removing one atom of hydrogen from the simplest hydrocarbon, methane, CH_4, the remaining univalent group, CH_3, can combine with another, yielding CH_3-CH_3, or C_2H_6, ethane or dimethyl. Here, again, an hydrogen atom may be replaced by the group CH_3, resulting in the compound $CH_3-CH_2-CH_3$, propane. The structure of these derivatives may be more clearly represented graphically:—



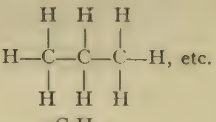
$$\begin{array}{c} H \\ | \\ H-C-H \\ | \\ H \end{array}$$

CH_4



$$\begin{array}{cccc} & H & H & \\ & | & | & \\ H- & C- & C- & H \\ & | & | & \\ & H & H & \end{array}$$

C_2H_6



$$\begin{array}{ccccc} & H & H & H & \\ & | & | & | & \\ H- & C- & C- & C- & H, \text{ etc.} \\ & | & | & | & \\ & H & H & H & \end{array}$$

C_3H_8

By continuing this chain-like union of the carbon atoms, there arises an entire series of hydrocarbons:—

$CH_3 - CH_2 - CH_2 - CH_3$ C_4H_{10} $CH_3 - CH_2 - CH_2 - CH_2 - CH_3$, etc. C_5H_{12}

The compounds constituting such a series are said to be *homologous*.

The composition of such an homologous series can be expressed by a general *empiric* or *rational* formula. The series formula for the marsh gas or methane hydrocarbons is C_nH_{2n+2}.

Each member differs from the one immediately preceding and the one following, by CH_2. The phenomenon of homology is therefore due to the linking power of the quadrivalent carbon atoms.

In addition to the hydrocarbons forming such a series, many others exist, *e. g.*, the monohydric alcohols, the aldehydes and monobasic acids:—

$C_nH_{2n+2}O$	$C_nH_{2n}O$	$C_nH_{2n}O_2$
CH_4O—methyl alcohol	CH_2O—formaldehyde	CH_2O_2—formic acid
C_2H_6O—ethyl alcohol	C_2H_4O—acetaldehyde	$C_2H_4O_2$—acetic acid
C_3H_8O—propyl alcohol	C_3H_6O—propionaldehyde	$C_3H_6O_2$—propionic acid
$C_4H_{10}O$—butyl alcohol	C_4H_8O—butyraldehyde	$C_4H_8O_2$—butyric acid.

Carbon compounds, alike chemically, but differing from each other in composition by a difference other than nCH_2, *e. g.*, the saturated and unsaturated hydrocarbons, form *isologous* series, according to Gerhardt:

$$\begin{array}{c} C_2H_6 - C_2H_4 - C_2H_2 \\ C_3H_8 - C_3H_6 - C_3H_4 \end{array}$$

Isomerism: Polymerism; Metamerism; Chain or Nucleus Isomerism; Position or Place Isomerism.—The view once prevailed that bodies of different properties must necessarily possess a different composition. The first hydrocarbons, showing that this opinion was erroneous, were discovered in 1820.

Liebig, in 1823, demonstrated that silver cyanate and fulminate were identical. In 1825 Faraday found in a compressed gas a liquid hydrocarbon having the same composition as gaseous ethylene. In 1828 Wöhler changed ammonium cyanate to urea, and in 1830 Berzelius established the similarity of tartaric acid and racemic acid.

Berzelius, in 1830, designated as *isomerides* (*ἰσομερής*) bodies of similar composition, but different in properties. A year later he distinguished two kinds of isomerism, viz., isomerism of bodies of different molecular mass—*polymerism*, and bodies of like molecular mass—*metamerism*.

Numerous isomeric carbon derivatives were discovered in rapid succession, hence an answer as to the question what causes isomeric phenomena acquired importance for the development of organic chemistry. The deeper insight into the structure of carbon compounds, which was gradually attained, gave rise in consequence to a further division of metameric phenomena.

The expression *metamerism* was employed to designate that kind of isomerism which is due to the homology of radicals held in combination by atoms of higher valence. If the homologous radicals are joined by polyvalent elements, then those compounds are metameric, in which the sum of the elements, contained in the radicals, is the same (H may be viewed as the simplest radical):

$$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O \quad \text{is metameric with} \quad \left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\}O$$

Ethyl Alcohol. Methyl Ether.

$$\left.\begin{matrix}C_3H_7\\H\end{matrix}\right\}O \quad \text{is metameric with} \quad \left.\begin{matrix}C_2H_5\\CH_3\end{matrix}\right\}O$$

Propyl Alcohol. Ethyl Methyl Ether.

$$\left.\begin{matrix}C_2H_5\\H\\H\end{matrix}\right\}N \quad \text{is metameric with} \quad \left.\begin{matrix}CH_3\\CH_3\\H\end{matrix}\right\}N$$

Ethylamine. Dimethylamine.

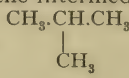
$$\left.\begin{matrix}C_3H_7\\H\\H\end{matrix}\right\}N \quad \text{is metameric with} \quad \left.\begin{matrix}C_2H_5\\CH_3\\H\end{matrix}\right\}N \quad \text{and} \quad \left.\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\right\}N$$

Propylamine. Ethyl Methylamine. Trimethylamine.

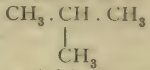
The constitution of the radicals in this division was disregarded, the type formulas were sufficiently explanatory. We have recognized the power of the quadrivalent carbon atoms to unite in a chain-like manner as the cause of homology, and to this cause may be attributed other phenomena of isomerism, which are not properly included under metamerism.

In deducing the formulas of the five simplest hydrocarbons of the homologous series C_nH_{2n+2}, the ethane formula $CH_3 . CH_3$ was developed from that of methane CH_4, and the propane formula $CH_3.CH_2.CH_3$ from the ethane formula C_2H_6. In the case of propane *intermediate* and *terminal* carbon atoms are distinguished. The former are attached on either side to two other carbon atoms, still possessing two valence units which are saturated by two hydrogen atoms. The terminal carbon atoms are linked to three hydrogen atoms.

With the next member of the series we observe a difference. Above, the fact that an hydrogen of the terminal methyl group of propane was replaced by methyl was the only condition considered. This led to the formula $CH_3 . CH_2 . CH_2 . CH_3$. However, the CH_3-group might replace an hydrogen atom of the intermediate CH_2-group, and then the result would be the formula $CH_3.\underset{\underset{CH_3}{|}}{CH}.CH_3$. In this hydrocar-



bon there is a *branched* carbon chain. The hydrocarbon with a continuous chain is termed *butane;* its isomeride is *isobutane*—

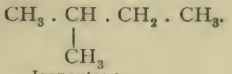


$$\begin{array}{c}CH_3 . CH . CH_3\\ |\\ CH_3\end{array}$$

Theoretically, by a similar deduction, the two butanes yield three isomeric pentanes:

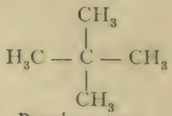
$CH_3 . CH_2 . CH_2 . CH_2 . CH_3$

Normal Pentane.



$$\begin{array}{l}CH_3 . CH . CH_2 . CH_3.\\ \quad\;\; |\\ \quad\; CH_3\end{array}$$

Isopentane.



$$\begin{array}{c}CH_3\\ |\\ H_3C - C - CH_3\\ |\\ CH_3\end{array}$$

Pseudopentane
Tetramethyl Methane.

These hydrocarbons are really known.

The number of possible isomerides increases rapidly with the increase in carbon atoms (B. **27**, R. 725).

The cause of isomerism in the homologous paraffins, as in so many other cases, is the different constitution of the carbon chain. The isomerism caused by a difference in linking, by the different structure of the carbon nucleus or the carbon chain, is termed nucleus or chain isomerism.

The investigation of the substitution products of the paraffin hydrocarbons brings to light another kind of isomerism. The principle of similarity of the four valences of a carbon atom renders logical and possible but one monochlor substitution product of methane and ethane. The same consideration which heretofore recognized the possibility of two methyl substitution products of propane, the two butanes possible by theory, leads to the possibility of two monochlor-propanes, dependent upon whether the chlorine atom has replaced the hydrogen of a terminal or intermediate carbon atom:

$CH_3 . CH_2 . CH_2Cl$
Normal Propyl Chloride.

$CH_3 . CHCl . CH_3$
Isopropyl Chloride.

If two hydrogen atoms of one of the carbon atoms of propane be replaced by an oxygen atom, the following case of isomerism arises:

$CH_3 . CH_2 . CHO$
Propyl Aldehyde.

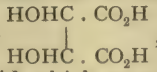
$CH_3 . CO . CH_3$
Acetone.

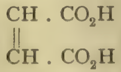
In the case of the two known chlorpropanes, and also in the case of propyl aldehyde and acetone, the cause of the isomerism is not due to difference in constitution of the carbon chain, but to the different *position* of the chlorine atoms with reference to the oxygen atoms of the same carbon chain. Isomerism, induced by the different arrangement or position of the substituting elements in the same carbon chain, is designated isomerism of *place* or *position*.

The intimate relationship of the two varieties of isomerism is apparent from the derivation of the ideas of nucleus or chain isomerism and *place* or *position* isomerism.

Recent Views Pertaining to the Structural Theory.—The theory of atomic linking not only revealed an insight into the causes of innumerable isomeric phenomena, but predicted unknown instances and determined their number in a very definite manner. In many cases isomeric modifications, possible by theory, were discovered at a later period. For certain isomerides, however, at first few in number, the structural formulas deduced from their synthetic and analytical reactions were insufficient, inasmuch as different compounds were known, to which the same structural formula could be given. The greatest similarity in reactions indicative of the structure was combined with a pre-eminently absolute difference in physical properties of the compounds belonging in this class. The tendency at first was to designate such bodies *physical isomerides*, meaning thereby an aggregation of varying complexes of chemically similar molecules.

The following groups of such isomerides have been well investigated:

1. The *four symmetrical dioxysuccinic acids:*  $\begin{array}{l} HOHC\,.\,CO_2H \\ \vert \\ HOHC\,.\,CO_2H \end{array}$, the ordinary or dextrotartaric acid, and racemic acid which were proved to be isomeric in 1830 by Berzelius. To these were added, through Pasteur's classic researches, lævo-tartaric and the inactive or meso-tartaric acids.

2. The *two symmetrical ethylene dicarboxylic acids*:  $\begin{array}{l} CH\,.\,CO_2H \\ \Vert \\ CH\,.\,CO_2H \end{array}$, fumaric and maleic acids.

3. The *three a-oxypropionic acids:* $CH_3\,.\,CH\,.\,OH\,.\,CO_2H$—inactive lactic acid of fermentation and sarcolactic acid. To these, lævolactic acid has been recently added.

Substances are included among these compounds, which liquified, either fused or in solution, turn the plane of polarization either to the right or left. The direction of deviation is indicated by prefixing "dextro" or "lævo" to the name of the bodies thus acting. Such carbon compounds are "optically active" in contradistinction to the other almost numberless derivatives which exert no influence on polarized light and are "optically inactive" or "inactive."

A direct synthesis of optically active carbon compounds has not yet been achieved, although optically inactive bodies have been synthesized. Pasteur has discovered methods by means of which the latter can be resolved into their components, which rotate the plane to an equal degree but in opposite direction. Upon splitting sodium-ammonium racemate into sodium-ammonium lævo- and dextro-tartrates Pasteur observed that the crystals of these salts manifested hemihedrism; that they behaved as an object and its image toward each other; and that like layers of equally concentrated solutions of these salts, at like temperature, deviated the plane of polarized light to an equal degree in opposite directions.

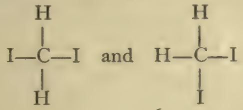
In 1860 Pasteur expressed himself as follows upon the cause of these phenomena—upon molecular asymmetry: "Are the atoms of the dextro-acid grouped in the form of a dextro-gyratory spiral, or are they arranged at the angles of an irregular tetrahedron, or are they distributed according to some other asymmetric arrangement? We know not. Undoubtedly, however, we have to do with an asymmetric arrangement, the images of which cannot mutually cover each other. It is not less certain that the atoms of the lævo-acid are arranged in opposite order." In 1873 J. Wislicenus added this comment to the evidence of similar structure in the optically inactive lactic acid of fermentation and the optically active sarcolactic acid: "Facts compel us to explain the difference of isomeric molecules of like structural formula by a difference in arrangement of the atoms in space." How the spacial configuration of the molecules of carbon compounds was to be represented was answered almost simultaneously and independently of each other by van 't Hoff and Le Bel (1874) (B. 26, R. 36). To do this they introduced the hypothesis of the asymmetric carbon atom. This hypothesis is the basis of the chemistry of space or stereochemistry of the carbon atom.

The hypothesis of an asymmetric carbon atom* is chiefly designed to explain optical activity and the isomerism of optically active carbon compounds.

While the theory of atomic linking abstains from any representation of the spacial arrangement of the atoms combined with each other to form a molecule, the experiences gathered from the investigation of simple carbon compounds demonstrate that definite spacial position-relations do not harmonize with actual facts. Assuming that the four valences of a carbon atom act in a plane and in perpendicular directions upon each other, the following possible isomerides for methane are evident:

No isomerides of the types CH_3R^1 and $CH(R^1)_3$
Two " " " " $CH_2(R^1)_2$, $CH_2R^1R^2$, $CHR^2(R^1)_2$,
Three " " " " $CHR^1R^2R^3$.

Methylene iodide, for example, should appear in two isomeric modifications:



$$\begin{array}{c}H\\|\\I-C-I\\|\\H\end{array}\quad\text{and}\quad\begin{array}{c}H\\|\\H-C-I\\|\\I\end{array}$$

However, two isomerides of no single disubstitution product of methane have been found; consequently, it is very improbable that the four affinities of a carbon atom are disposed in the manner indicated above. The carbon atom-models of Kekulé represent the carbon atom as a black sphere and the quadrivalence of it by four needles of equal length and firmly attached to the sphere (Baeyer terms them axes). These needles are not perpendicular to each other, nor do

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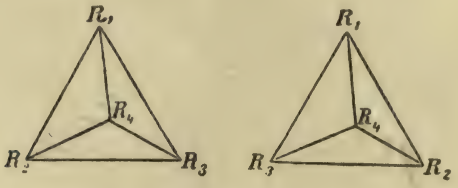
* Pasteur: Recherches sur la dissymétrie moléculaires des produits organiques naturels. Leçons de chimie professées en 1860. Paris, 1861. Vgl. Ostwald's Klassiker der exacten Wissenschaften, Nr. 28: Ueber die Asymmetrie bei natürlich vorkommenden organischen Verbindungen, von Pasteur. Uebersetzt und herausgegeben von M. und A. Ladenburg. J. H. van 't Hoff: Dix années dans l'histoire d'une théorie, 1887. K. Auwers: Die Entwickelung der Stereochemie, Heidelberg, 1890. A. Hantzsch: Grundriss der Stereochemie, Breslau, 1893. C. A. Bischoff: Handbuch der Stereochemie, 1893.

they lie in the same plane, but are so arranged that planes placed about their terminals produce a regular tetrahedron. van 't Hoff's generalizations are based upon this model: their fundamentals will be more fully developed in the following pages.

On the assumption that the affinities of a carbon atom are arranged like the summits of a regular tetrahedron, in the center of which there is the carbon atom, there would be no imaginable isomerides coinciding with $CH_2(R^1)_2$, $CH_2R^1R^2$, $CHR^2(R^1)_2$, but a case $CHR^1R^2R^3$ or the more general $CR^1R^2R^3R^4$—an isomeric phenomenon of peculiar nature—might be predicted. A carbon atom of this description—one that is connected with four different univalent atoms or atomic groups—van 't Hoff has designated an *asymmetric carbon atom*, proposing to represent it by an italic *C*. It is sometimes indicated by a small star.

If a compound contains an asymmetric carbon atom we can conceive of its existence in two isomeric modifications, the one being an image of the other:

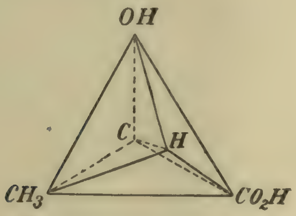


These spacial arrangements are more fully understood by the aid of the models suggested by Kekulé, van 't Hoff, and others than by their projection upon the flat surface of paper. van 't Hoff introduced tetrahedron models in which the solid angles were colored; this was to represent and indicate different radicals. They lack this advantage, possessed by the Kekulé model, that the carbon atom has entirely disappeared from the model. It must be imagined as being in the center of the tetrahedron, and in projections of these models (see above) the radicals are united to each other by lines, the latter, however, not in any sense representing a chemical union.

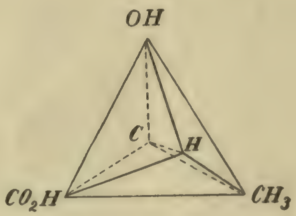
In the left tetrahedron the successive series $R^1R^2R^3$ proceeds in a direction directly opposite to that of the hand of a watch, while in the right tetrahedron the course coincides with that of the hand. The two figures cannot, by rotation, be by any means brought into the same position,—that is, in a position to cover each other completely,—any more than the left hand can be made to cover the right, or a picture its image or reflection.

The Isomerism of Optically Active Carbon Compounds.—The cause of optical activity, in the opinion of van 't Hoff and of Le Bel, is the presence of one or several asymmetric carbon atoms in the molecule of every optically active body. It is obvious that two molecules which only differ in that the series of atoms or atomic groups attached to an asymmetric carbon atom differ successively in order of arrangement, which therefore are identical in chemical structure, must be so similar in chemical properties as to give rise to confusion. However, those physical properties, upon which the opposite successive series of atoms or atomic groups in union with asymmetric carbon exerts an influence, *e. g.*, the power of deviating the plane of polarized light, must be equal in value, but as regards the prefix they are opposite. The union of two molecules identical in structure, having equal but opposite rotatory power, gives rise to a molecule of an optically inactive polymeric compound.

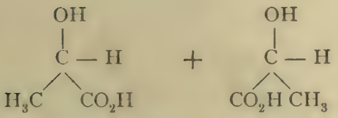
Compounds Containing an Asymmetric Carbon Atom.—*a* Oxypropionic acid, $CH_3—{*}CHOH\ .\ CO_2H$, has been brought forward as an example of a compound, containing one asymmetric carbon atom. It can appear in two optically active, structurally identical, but physically isomeric and one optically inactive, structurally identical polymeric modifications:



Dextro-lactic Acid.
(Sarcolactic Acid.)



Lævo-lactic Acid.



{ (+) d-Lactic Acid (—) l-Lactic Acid } = Lactic Acid of Fermentation or Inactive Lactic Acid.

The following compounds also contain one asymmetric carbon atom:

Leucine,	$C_4H_9\ {*}CHNH_2.\ CO_2H$
Malic Acid,	$CO_2H.\ CH_2.\ {*}CH\ OH.\ CO_2H$
Asparagine,	$CO\ NH_2.\ CH_2.\ {*}CHNH_2.\ CO_2H$
Mandelic Acid,	$C_6H_5.\ {*}CH.OH.\ CO_2H$
Conine,	$CH_2{<}\begin{matrix}CH_2—{*}CH—(C_3H_7)\\CH_2—CH_2\end{matrix}{>}NH$

Each of the preceding bodies is known in two optically active and one optically inactive modifications.

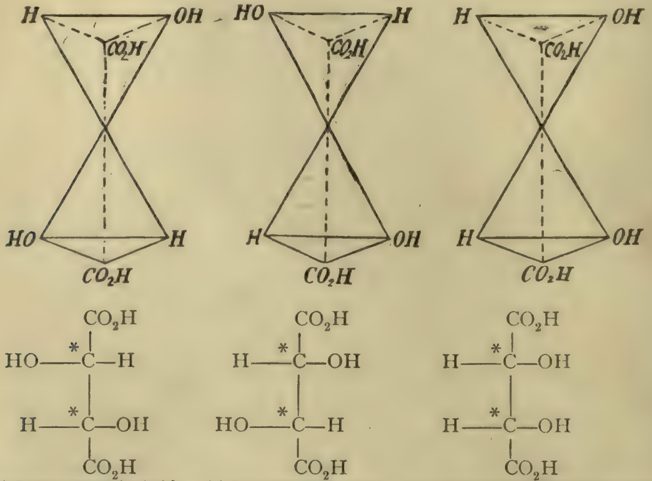
Compounds Containing Two Asymmetric Carbon Atoms.—The relations are more complicated when two carbon atoms are present.

The simplest case would then be that in which similar or like groups are in union with the two asymmetric carbon atoms. The one-half of the molecule would be constructed chemically just like the other half. The four isomeric dioxysuccinic acids belong in this group. This group of so-called tartaric acids has become of the greatest importance in the development of the chemistry of optically active carbon derivatives.

They were the first to be most carefully investigated chemically, optically, and crystallographically, and were used by Pasteur in the development of methods for the splitting-up of the optically inactive compounds into their optically active components (p. 65). Their importance was increased in addition by the fact that they were brought into an intimate genetic relation with fumaric and maleic acids —two isomeric bodies which will be considered in the next section (p. 50).

Should a carbon compound contain two asymmetric carbon atoms united to similar groups then to the three isomeric modifications which a compound containing one asymmetric carbon atom is capable of forming comes a fourth possibility. If the groups linked to one asymmetric carbon atom, viewed from the line of union of the two asymmetric carbon atoms, show an opposite successive arrangement to that of the other asymmetric carbon atom, an inactive compound results, due to an *intramolecular compensation:* the action due to the one asymmetric atom upon polarized light will be canceled by an equally great, but opposite action caused by the other asymmetric carbon atom.

The hypothesis of the asymmetric carbon atom gave the first and, indeed, the only satisfactory explanation for the occurrence of four isomeric symmetrical dioxysuccinic acids. The following formulas represent these four acids:



$$\begin{array}{c}CO_2H\\ |\\ HO—\overset{*}{C}—H\\ |\\ H—\overset{*}{C}—OH\\ |\\ CO_2H\end{array}\qquad\begin{array}{c}CO_2H\\ |\\ H—\overset{*}{C}—OH\\ |\\ HO—\overset{*}{C}—H\\ |\\ CO_2H\end{array}\qquad\begin{array}{c}CO_2H\\ |\\ H—\overset{*}{C}—OH\\ |\\ H—\overset{*}{C}—OH\\ |\\ CO_2H\end{array}$$

(1) Dextrotartaric Acid. (2) Lævotartaric Acid. (3) Inactive or Mesotartaric Acid.
Dextrotartaric Acid + Lævotartaric Acid = (4) Racemic Acid.

The possibilities of isomerism with carbon compounds containing more than two asymmetric carbon atoms—a condition observable with the polyhydric alcohols, their corresponding aldehyde alcohols, and ketone alcohols (the simplest sugar varieties), as well as with their oxidation products, will be more elaborately discussed under these several groups of compounds.

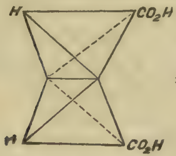
Geometrical Isomerism, Stereoisomerism in the Ethylene Derivatives (*Alloisomerism*).—Two carbon atoms singly linked to each other whose valences, not required for mutual union, hold other atoms or atomic groups, should be considered as able to rotate independently of each other about their axis of union. J. Wislicenus assumes, however, that the atoms or atomic groups combined with these two carbon atoms exercise alternately a "directing influence" upon each other until finally the entire system has passed into the "favorable configuration" or the "preferred position." It follows from this assumption that, in ethane derivatives in which asymmetric carbon atoms are not present, structurally identical isomerides cannot occur. When the van 't Hoff tetrahedron models are employed to represent two systems united to each other by carbon atoms singly linked then the two systems rotating independently of each other about a common axis move each in the solid angle of a tetrahedron (compare the projection-formula of the tartaric acids shown above).

A different state prevails where the carbon atoms are doubly linked. The double union, according to van 't Hoff, prevents a free and independent rotation of the two systems and space-isomerides are possible.

The tetrahedron models represent this double union in such a manner that two tetrahedra have two summits in common and arrange themselves about a common edge. The differences in chemical deportment of this class of isomerides are frequent and important. They are to be attributed to the greater or less spacial removal of the atomic groups, which determine the chemical character.

Compounds having the common formulas $abC = Cab$ or $abC = Cac$, may exist in two isomeric modifications. In one instance groups of like name are directed toward the same side—according to J. Wislicenus the "plane symmetric configuration"—or they are directed toward opposite sides—then they have according to the same author the central or axially symmetric configuration. Baeyer suggests for this form of asymmetry the term "relative asymmetry" in contradistinction to the kind of asymmetry which substances with asymmetric carbon atoms show ; the latter he prefers to call "absolute asymmetry." The structurally symmetric ethylene dicarboxylic acid is the most striking example of this class of isomerism. It exists in two isomeric modifications. They are fumaric and maleic acids. Both have been very carefully investigated. Maleic acid readily passes into an anhydride, hence the plane symmetric configuration is ascribed to it. Fumaric acid does not form an anhydride ; to it is given the axial symmetric configuration. In this the two carboxyl groups are as widely removed from each other as possible. In projection formulas and in structural formulas, to which there is given a spacial aspect, the configuration of these two acids would be represented in the following way:

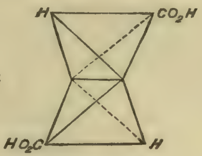
1



$$= \begin{array}{l} HC.CO_2H \\ \| \\ HC.CO_2H \end{array}$$

Maleïc Acid.
Plane Symmetric
Configuration.

2



$$= \begin{array}{r} HO_2C.CH \\ \| \\ HC.CO_2H \end{array}$$

Fumaric Acid.
Central or Axially Symmetric
Configuration.

The isomerism of mesaconic and citraconic acids, $(CH_3)\ (CO_2H)\ C = CH\ (CO_2H)$, is of the same class; the first acid corresponds to fumaric acid and the second to maleïc acid. Further examples of the class are:

Crotonic and Isocrotonic Acids, .	$CH_3\ CH:CHCO_2\ H$.
Angelic and Tiglic Acids, . . .	$CH_3.\ CH:C\ (CH_3)\ CO_2H$.
Oleic and Elaïdic Acids, ...	$C_{15}\ H_{31}\ CH:CHCO_2H$.
Erucic and Brassidic Acids, . . .	$C_8\ H_{17}\ CH:CH.\ C_{11}\ H_{22}.\ CO_2H$.
The two α-Chlorcrotonic Acids, .	$CH_3.\ CH:CCl.\ CO_2H$.
“ “ β-Chlorcrotonic Acids, .	$CH_3.\ CCl:CH.\ CO_2H$.
“ “ Tolane Dichlorides, . .	$C_6H_5\ CCl:CCl\ C_6\ H_5$.
“ “ “ Dibromides, . .	$C_6\ H_5\ CBr:CBr\ C_6\ H_5$.
“ “ o-Dinitrostilbenes, . . .	$NO_2\ [2]\ C_6\ H_4\ [1]\ CH:CH\ [1]\ C_6\ H_4\ ]2]\ NO_2$.
Cinnamic and Allocinnamic Acids,	$C_6\ H_5.\ CH:CH\ CO_2H$.
The two α-Bromcinnamic Acids,	$C_6\ H_5.\ CH:CBr\ CO_2H$.
“ . “ β-Bromcinnamic “	$C_6\ H_5.\ CBr:CH\ CO_2H$.
“ “ Coumaric “	$HO\ [2]\ C_6\ H_4\ [1]\ CH:CH.\ CO_2H$, etc.

Isomeric phenomena of this kind Michael designates *allo-isomerism*: he connects with it, however, no assumption as to its cause. When, upon the application of heat, a body passes into a more stable modification Michael prefixes "allo" to the name of the more stable form; thus, fumaric acid is allomaleïc acid (B. **19**, 1384).

Fumaric and maleïc acids are placed at the head of this class of isomeric phenomena not only because they have been most thoroughly investigated, but chiefly because the two optically inactive dioxytartaric acids bear to them an intimate genetic relation (p. 48). Kekulé and Anschütz showed that by potassium permanganate fumaric acid was converted into racemic acid, and maleïc acid into mesotartaric acid. This conversion harmonizes beautifully with the van 't Hoff–Le Bel conception of these acids; indeed, it might have been predicted. These relations will be more fully elaborated in the discussion of the four acids. In studying maleïc and the alkylmaleïc acids, the thought will be expressed that in all probability a structure differing widely from that assigned fumaric acid properly falls to maleïc acid and its derivatives.

The structure will be influenced by the configuration. The relations are similar in the case of the coumaric acids (see these).

Baeyer considers that the isomerism of the saturated iso- or carbocyclic compounds, as will be more fully explained when the hexahydrophthalic acids are described, bears a definite relation to the stereo-isomerism of the ethylene derivatives. The same author maintains that the simple ring-union of carbon atoms viewed from a stereochemical standpoint has the same signification as the double union in open chains. Therefore, stereo-isomerism in the carbon compounds with double union would appear merely as a special case of isomerism in simple ring-unions. Baumann applied this idea to saturated heterocyclic compounds—to the polymeric thioaldehydes (see these).

Baeyer suggested the introduction of a common symbol for all geometrical isomerides; it was the Greek letter Γ. The addition of an index will enable one to readily express the kind of isomerism. In the case of compounds which contain absolute asymmetric carbon atoms, the signs $+$ $-$ can be employed. Thus the expressions

$$\left.\begin{array}{lll} \text{Dextro-tartaric Acid} & = \Gamma + + \\ \text{Laevo-}\quad \text{``}\quad\ \ \text{``} & = \Gamma - - \\ \text{Mesotartaric}\quad\ \ \text{``} & = \Gamma + - \end{array}\right\} \text{Tartaric Acid}$$

are understood without special explanation. In the case of relative asymmetry in unsaturated compounds and saturated rings, Baeyer proposes to use the terms *cis* and *trans*. Maleïc Acid $= \Gamma$cis, cis or briefly Γcis ethylene dicarboxylic acid, while fumaric acid $= \Gamma$cis, trans ethylene dicarboxylic acid.

The ready formation of iso- or carbocyclic and heterocyclic compounds has been attributed to the spacial arrangement of the atoms, in case that five or six atoms take part in the ring formation.

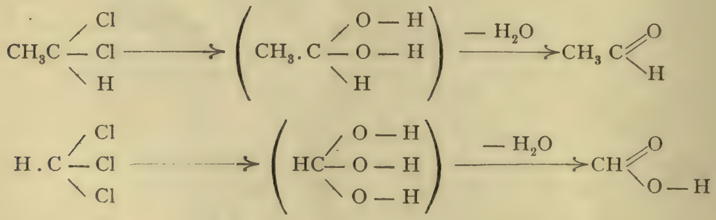
Such stereochemical considerations will be duly observed in the introduction to the iso- or carbocyclic compounds, as well as in the introduction to the heterocyclic derivatives, and in the discussion of the cyclic carboxylic esters or lactones, the cyclic acid amides or lactams, the anhydrides of dibasic acids, etc.

Hypotheses Relating to Multiple Unions of Carbon.—The multiple unions of carbon are important in stereochemical considerations, hence there has not been a lack of search into the nature of this union as well as attempts to represent it. All investigations in this direction demonstrate how difficult it is at present to understand so obscure a force as chemical attraction or affinity resting upon a mechanical basis. Despite the demand and necessity that may exist for the introduction of hypotheses dealing with the mechanics of multiple linkage the views thus far presented are in many essentials contradictory and not one has won general recognition for itself. See Baeyer, B. **18**, 2277; **23**, 1274; Wunderlich, Configuration organischer Molecüle, Leipzig (1886); Lossen, B. **20**, 3306; Wislicenus, B. **21**, 581; V. Meyer, B. **21**, 265 Anm.; **23**, 581, 618; V. Meyer und Riecke, B. **21**, 946; Auwers, Entwicklung der Stereochemie (Heidelberg 1890), p. 22–35; Naumann, B. **23**, 477; Brühl, A. **211**, 162, 371; Deslisle, A. **269**, 97; Skraup, Wien. Monatsh. **12**, 146.

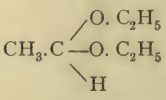
Stereochemistry of Nitrogen.—Isomeric phenomena of nitrogen-containing compounds of like chemical structure, which could not be ascribed to the same cause as prevailed in carbon compounds, led to the transference of stereochemical views to the nitrogen atom. There appeared to be an "absolute nitrogen asymmetry" corresponding to the "absolute carbon asymmetry." Examples of this class existed according to Le Bel in the unstable, optically active modification of methyl-ethyl-propyl-isobutyl-ammonium chloride (C. r. **112**, 724).

The isomerisms of the oximes, according to Hantzsch and Werner, and those of the hydroxamic acids, according to Werner, correspond to the "relative asymmetry" that the doubly-linked carbon atoms are capable of causing.

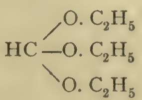
Intramolecular Atomic Rearrangements.—Many investigations have shown that certain modes of linking, apparently possible from a valence standpoint, cannot, in fact, occur, or when they do take place are possible only under certain definite conditions. In reactions, for example, in which two or three hydroxyl groups should unite with the same carbon atom, a splitting-off of water almost invariably occurs and oxygen unites doubly with carbon, *e. g.*,



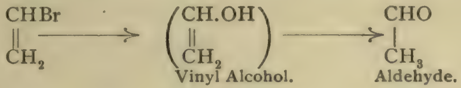
On the other hand, the ethers derivable from these unstable "alcohols" are stable:



and

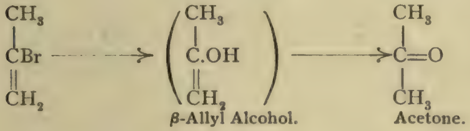


In other cases there is a splitting-off of an halogen hydride, water or ammonia with the production of an unsaturated body, or an anhydride of a dibasic acid, or a cyclic ester (a *lactone*), or a cyclic amide (a *lactam*). In these reactions two molecules result from one molecule, in which atom-groups occur in unstable linkage-relations. Together with the organic molecule there is formed a simple inorganic body. However, this course is not the only possible direction of change. On the contrary, by intramolecular atom rearrangement, unstable atomic groupings pass in the moment of their formation into stable forms, the molecular magnitude at the same time not altering. The hydrogen atom especially is inclined to wander. This is also true of other groups: *alkyl* and *phenyl* groups. To-day the number of phenomena of this class is remarkably large. A few examples, however, will suffice. A free hydroxyl group adds itself in most cases to a carbon atom in double union with its neighboring carbon atom. When intramolecular atom-rearrangements occur the hydrogen of the hydroxyl attaches itself to the adjacent carbon atom, and oxygen of hydroxyl unites doubly with carbon (Erlenmeyer's rule, B. **13**, 309; **25**, 1781).



$$\begin{array}{l}CHBr\\ \|\\ CH_2\end{array} \longrightarrow \left(\begin{array}{l}CH.OH\\ \|\\ CH_2\end{array}\right) \longrightarrow \begin{array}{l}CHO\\ |\\ CH_3\end{array}$$

Vinyl Alcohol. Aldehyde.

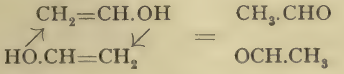


$$\begin{array}{l}CH_3\\ |\\ CBr\\ \|\\ CH_2\end{array} \longrightarrow \left(\begin{array}{l}CH_3\\ |\\ C.OH\\ \|\\ CH_2\end{array}\right) \longrightarrow \begin{array}{l}CH_3\\ |\\ C{=}O\\ |\\ CH_3\end{array}$$

β-Allyl Alcohol. Acetone.

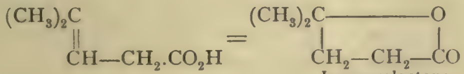
However, the ethers obtained from vinyl alcohol (see this) are stable: $CH_2{=}CHO.C_2H_5$ and $CH_2{=}C(O.C_2H_5){-}CH_3$ are known.

It may also be imagined that a transposition such as that described above can occur by two unstable and similar molecules rearranging with each other, so that two similar stable molecules result:



$$\begin{array}{l}CH_2{=}CH.OH\\ \nearrow \qquad\quad \swarrow\\ HO.CH{=}CH_2\end{array} = \begin{array}{l}CH_3.CHO\\ \\ OCH.CH_3\end{array}$$

An elevation of temperature is necessary to induce many of these reactions. Both compounds are capable of existence. Unsaturated acids pass into lactones. The intramolecular atom-rearrangement proceeds in a direction favoring the formation of a stable ring:



$$\begin{array}{l}(CH_3)_2C\\ \quad\|\\ \quad CH{-}CH_2.CO_2H\end{array} = \begin{array}{l}(CH_3)_2C{-}{-}{-}{-}O\\ \quad | \qquad\qquad\; |\\ \quad CH_2{-}CH_2{-}CO\end{array}$$

Isocaprolactone.

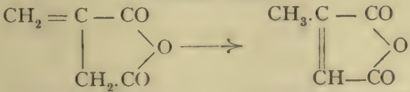
In other unsaturated compounds we observe that the unsymmetrical is transformed into a symmetrically formed body through the rearrangement of the double linking of carbon:

$$CH_2:CH.CH_2I \xrightarrow{KCN} CH_2:CH.CH_2.CN \longrightarrow CH_3.CH:CH.CN \longrightarrow$$

Allyl Iodide. Nitrile of Crotonic Acid.

$$CH_3.CH:CH.CO_2H$$

Crotonic Acid.



$$\begin{array}{l}CH_2{=}C{-}CO\\ \quad\;\; | \qquad \searrow\\ \quad\;\; | \qquad\;\; O\\ \quad\;\; | \qquad \nearrow\\ \quad CH_2.CO\end{array} \longrightarrow \begin{array}{l}CH_3.C{-}CO\\ \quad\;\; \| \qquad \searrow\\ \quad\;\; \| \qquad\;\; O\\ \quad\;\; \| \qquad \nearrow\\ \quad CH{-}CO\end{array}$$

Itaconic Anhydride. Citraconic Anhydride.

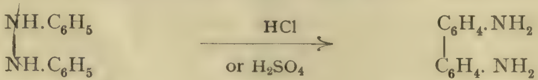
The esters of hydrosulphocyanic acid, under the influence of heat, rearrange themselves into the isomeric mustard oils, sulphur unites doubly with carbon and the alcohol radical that had previously been in union with sulphur links itself to nitrogen:

$$\underset{\text{Allyl Sulphocyanide.}}{C_3H_5-S-C\equiv N} \longrightarrow \underset{\text{Allyl Mustard Oil.}}{S=C=N.C_3H_5}$$

Isonitriles or carbylamines, when heated, pass into nitriles; the alcohol radical previously in union with nitrogen, wanders over to carbon:

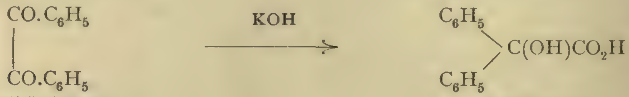
$$\underset{\text{Phenyl Carbylamine.}}{C_6H_5-N=C} \longrightarrow \underset{\text{Benzonitrile.}}{C_6H_5-C\equiv N.}$$

Other rearrangements among the atoms of compounds only transpire as the result of the action of an energetic acid or a powerful base. Indifferent bodies pass over into basic and acid compounds:



$$\begin{array}{l} NH.C_6H_5 \\ | \\ NH.C_6H_5 \end{array} \xrightarrow[\text{or } H_2SO_4]{HCl} \begin{array}{l} C_6H_4.NH_2 \\ | \\ C_6H_4.NH_2 \end{array}$$

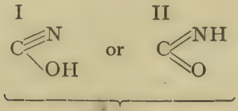
Hydrazobenzene (indifferent). Benzidine (diacid base).



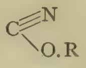
$$\begin{array}{l} CO.C_6H_5 \\ | \\ CO.C_6H_5 \end{array} \xrightarrow{KOH} \begin{array}{l} C_6H_5 \\ C_6H_5 \end{array} \!\!> C(OH)CO_2H$$

Benzil (indifferent). Benzilic Acid.

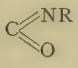
Pseudo-forms, Pseudomerism (Tautomerism, Desmotropy, Merotropy).—In most of the intramolecular rearrangements it was the hydrogen atoms that wandered. Alcohol radicals and phenyl groups are prone to do the same. It was in this way that a gradual knowledge that many groups were unstable and stable sprang up. In the case of many bodies it became to be known that apparently they could react in accordance with two different formulas. In other words, as our constitutional formulas were deduced from chemical deportment, it may be said that compounds existed to which two, and under certain circumstances more, constitutional formulas could be ascribed. Baeyer (B. **16**, 2188) explained this phenomenon in such a manner that the stable bodies, under heat influence or reagents, passed into unstable modifications. "These isomerides are only known in compounds; in the free state they revert to the original form. Their instability is referable to the mobility of the hydrogen atoms, since the replacement of the latter is followed by stability" (compare A. W. Hofmann, B. **19**, 2084). Mention may be here made of:



Cyanic Acid.



Known.



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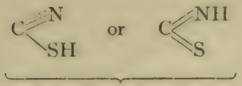
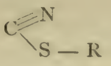


Hydrosulphocyanic Acid. Isothiocyanic Acid.



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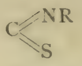
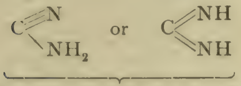
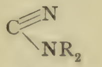


Known (mustard oils.)



Cyanamide. Carbodi-imide.



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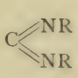

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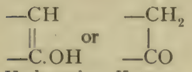
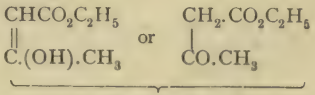


$$\begin{array}{c} -CH \\ \| \\ -C.OH \end{array} \text{ or } \begin{array}{c} -CH_2 \\ | \\ -CO \end{array}$$

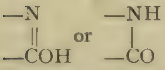
Hydroxyl or Enol Form. Ketone Form.

e. g.,



$$\begin{array}{l} CHCO_2C_2H_5 \\ \| \\ C.(OH).CH_3 \end{array} \text{ or } \begin{array}{l} CH_2.CO_2C_2H_5 \\ | \\ CO.CH_3 \end{array}$$

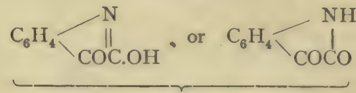
Acetoacetic Ester.



$$\begin{array}{c} -N \\ \| \\ -COH \end{array} \text{ or } \begin{array}{c} -NH \\ | \\ -CO \end{array}$$

Lactime Form. Lactam Form.

e. g.,



Isatine.

Baeyer proposes to represent the unstable modifications by the designation "*pseudo*." *Pseudomerism* is the term that will be adopted in this work for the phenomenon in which one and the same carbon compound can react in accordance with different structural formulas. The unstable form of a derivative will, therefore, take the name "pseudoform" or "pseudo-modification." In some instances both forms are known.

It is noteworthy that most "pseudomeric" compounds are acid in nature; they can form salts. When these salts are treated with alkylogens or acylhaloids the two classes of isomerides appear. H. Goldschmidt (B. **23**, 253) refers this phenomenon to the appearance of free ions. Hence in passing judgment upon questions of pseudomerism only those reactions can be considered, from which electrolytic dissociation is excluded. Michael (J. pr. Ch. **37**, 473) offers the thought (and it is worthy of every consideration) that in the transpositions of the salts by organic haloids two independent processes, depending on the conditions present, take place: there is a simple exchange in that the organic radical takes the place of the metal, or the radical haloid first adds itself and subsequently the metallic haloid separates. In the latter case the organic radical assumes a position different from that previously held by the metallic atom (compare acetoacetic ester and malonic ester). Nef has recently maintained the correctness of Michael's view.

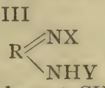
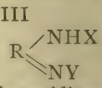
Laar, on the contrary (following Butlerow, A. **189**, 77, van 't Hoff, Ansichten über die organische Chemie **2**, 263, and Zincke, B. **17**, 3030), assumes that such compounds consist of a mixture of structural isomerides, in that an easily mobile hydrogen atom oscillates between two positions in equilibrio, and thereby the entire complex becomes mobile. He designates the phenomenon as *tautomery*. Discarding the uncertainty introduced into the classification of the carbon compounds by the acceptance of this view, it has been noted that carbon compounds which Laar considers mixtures of structurally isomeric bodies do not differ in their physical properties from carbon compounds which offer no place in their structure for this equivocal assumption. By the assumption of tautomerism with the underlying meaning assigned it by Laar, the experimental solution of the problem as to the conditions under which pseudo-forms are capable of existence is without object, although from the nature of the case the identification of easily alterable intermediate reaction-products must continue to be one of the most difficult problems, yet success has been met with in quite a number of cases. The indefatigable labors of Raoul Pictet, made with low temperatures, have brought to light splendid results. These are at the disposition of chemistry, and in the light of these new data the experiments relating to the determination of the conditions under which unstable modifications can exist, deserve to receive careful, renewed attention.

The preceding section was prepared in 1893. Since then, numerous confirmations of these views have been found. The *ketones* constitute the most important class of compounds, which are tautomeric according to Laar. In them, as in acetoacetic ester, the oscillation is between the ketone- and the hydroxyl formula or enol formula. That the ketone formula is present in acetoacetic ester (see this) may be accepted as established.

The investigations of Claisen (A. **291**, 25), of Guthzeit (A. **285**, 35), of W. Wislicenus (A. **291**, 147), and of Knorr (A. **293**, 70) have demonstrated that there exist compounds of the form $—C(OH) = \overset{|}{C}—CO—$, which readily pass into the form $—CO—\overset{|}{C}H—CO—$, and conversely are easily produced from the latter: "The character of the added residue, the temperature and the nature of the solvent, in the case of dissolved substances, determine which of the two forms will be the more stable." Claisen appears to think that the rearrangement of the group $R—CO—\overset{|}{C}H—$ into $R—C(OH) = \overset{|}{C}—$ will occur more readily, according as the radical $R—CO$ is more negative. He designates the acid enol-form the α-compound, and the neutral keto-form the β-body, *e. g.*,

α-Acetyldibenzoyl methane — $CH_3.C(OH) = C(COC_6H_5)_2$
β-Acetyldibenzoyl methane — $CH_3.CO —— HC(CO.C_6H_5)_2$.

To avoid misunderstandings or confusion it would be better to characterize the α-body by a name, expressing its constitution; thus, α-methyl-β-dibenzoyl-vinol. The determination of the molecular refractions (Brühl, J. pr. Ch. [2] **50**, 119) and of the magnetic rotations (W. H. Perkin, Sr.) is a most valuable aid in the chemical investigation of such isomerides.

While these readily introconvertible isomerides possess an entirely distinct chemical character and belong to different classes (alcohols or ketones), bodies exist which, according to their method of formation, appear in two modifications belonging to the same class, yet show themselves to be identical, *e. g.*, diazoamido-compounds, amidines and formazyl derivatives of the common types  $\overset{III}{R}\begin{smallmatrix}\diagup NX \\ \diagdown NHY\end{smallmatrix}$ and  $\overset{III}{R}\begin{smallmatrix}\diagup NHX \\ \diagdown NY\end{smallmatrix}$, in which R is similar to $\vdots$ N in the diazoamido-compounds, to $\vdots$ CH in the amidines, and to . N : CH. N : in the formazyl derivatives, while X and Y represent two different univalent hydrocarbon radicals. Knorr's methyl pyrazoie (see this) belongs in this category. Following the example of Kekulé (compare Constitution of Benzene) this phenomenon has been explained by *oscillations* or, as Knorr expressed it, by *floating linkings* (A. **279**, 188): the imide hydrogen atom is supposed to oscillate between two nitrogen atoms. Brühl proposes the name *phasotropy* for the phenomenon itself (B. **27**, 2396), while v. Pechmann designates it *virtual tautomerism* (B. **28**, 2362).

Akin to the idea of *pseudomerism* is the idea of *desmotropy*, derived from δεσμός, link, union, and τρέπειν, to change. (P. Jacobson, B. **20**, 1732 Anmerk.; **21**, 2628 Anmerk.; Hantzsch, B. **20**, 2802; **21**, 1754; Förster, B. **21**, 1857). Michael suggests the term *merotropy* (J. pr. Ch. [2] **45**, 581 Anm.; **46**, 208).

THE NOMENCLATURE OF THE CARBON COMPOUNDS.

The steadily increasing number of carbon derivatives has shown that definite principles should determine their designation. The absence of general and international rules where they were possible has led to great confusion in the nomenclature.

Compounds originating from plants and animals received names that indicated their origin, and often at the same time their characteristic chemical properties: Urea, uric acid, tartar, tartaric acid, formic, oxalic, malic, citric, salicylic acids, etc. With a large class of bodies, *e. g.*, the bases, glucosides, bitter principles, fats, etc., it was customary to employ the ending "ine": coniine, nicotine, guanidine, creatine, betaïne, salicine, amygdaline, glycerine, stearine, etc., and in the terminations al, ol, an, en, yl, ylene, ylidene, the effort was made to show the similarity of certain compounds, without, however, proceeding in a connected way.

The more thoroughly the constitution of bodies became known, the greater was the desire to express the manner in which the atoms were united by names. This was especially true in the case of isomeric compounds. The manner in which this was done, however, was left to the choice of the individual, and thus it happened that often one and the same derivative received different names, these being in substance identical.

Of the early suggestions on nomenclature that of Kolbe (A. 113, 307) on *carbinol* deserves special consideration. As is known, Kolbe referred the names of the monohydric, saturated alcohols back to the name *carbinol.* In order to make this principle more general, we should proceed as follows: Ascertain the carbinol or carbinols for each class of compounds—that is, find those bodies from which the homologues might be derived, just as the monohydric, saturated alcohols might be deduced from methyl alcohol or carbinol. Without attempting at this time to determine the limits of the "carbinol nomenclature," it will suffice to remark that in the case of the paraffin dicarboxylic acids all the normal homologues are the carbinols, if I may so call them; *e. g.*, malonic acid, succinic acid, normal glutaric acid, adipic acid, etc. Indeed, names such as monomethyl malonic acid, ethylmethyl malonic acid, symmetric and unsymmetric dimethyl succinic acid, etc., are so readily understood that they are really preferred, and are favorites with many chemists.

In 1892 representative chemists of various countries convened in Geneva for the purpose of discussing a nomenclature which would clearly express the constitution of a carbon derivative. The new names adopted by the Geneva Commission will, in the case of certain important series of compounds, be observed in the present text; they will be enclosed in brackets—*e. g.*, [ethene] for ethylene, [ethine] for acetylene, etc. The designations of the simpler bodies—the names justified from an historical standpoint and deduced from important reactions—will not be wholly eliminated. Thus, the names ethyl hydride, dimethyl or methyl methane will be used for ethane, depending upon what relations are to be especially emphasized.

The new nomenclature proceeds from, or begins with, the hydrocarbons. The name of the hydrocarbon serves as the *root* for the names of those substances which contain their carbon atoms arranged in a similar manner. The different classes of bodies are distinguished by the addition of suffixes to the names of the hydrocarbons. Alcohols end in *ol*, aldehydes in *al*, ketones in *on*, and the acids in *acid*—*e. g.*, [ethanol] = ethyl alcohol, [ethanal] = acetaldehyde, [propanon] = acetone, [propanal] = propionic aldehyde, [ethan-acid] = acetic acid. These examples will suffice. The more important suggestions will receive full consideration under the various classes of bodies, which are discussed. The principles of this nomenclature have already encountered difficulties, especially in attempting to indicate in name a compound having a mixed character—*e. g.*, the body $COH—CH_2—CHOH—CO—CO_2H$, which would be *pentanolalon-acid.* The accumulation of suffixes, each of which possesses a meaning peculiar to itself, has "conduit rapidement à des termes bizarres, d'une complication facheuse et d'une prononciation difficile" (Amé Pictet).

Compare F. Tiemann: Ueber die Beschlüsse des internationalen in Genf vom 19. bis 22. April 1892 versammelten Congresses zur Regelung der chemischen Nomenclatur, B. **26**, 1595. Ueber die Nomenclatur der ringförmigen Verbindungen, compare M. M. Richter, B. **29**, 586.

PHYSICAL PROPERTIES OF THE CARBON COMPOUNDS.

It can, in general, be foreseen that the physical as well as the chemical properties of carbon compounds must be conditioned by their composition and constitution. Such a regular connection has been, however, only determined for a few properties;

1. Crystalline form;
2. Specific gravity, density;
3. Melting point;
4. Boiling point;
5. Solubility;—serve chiefly for the external characterization of carbon derivatives, while (6) *optical properties*—(*a*) light refraction, (*b*) optical rotatory power—and (7) *electric conductivity* are important in studying constitution.

1. CRYSTALLINE FORM OF CARBON COMPOUNDS.

The crystalline form of a carbon derivative is one of its most important marks. By it the body may be recognized and distinguished from other substances. The preparation of organic substances in measurable forms, which could be fully determined, has been of the greatest importance in organic chemistry. *The crystalline forms of isomeric bodies are always different.* Many substances of organic nature can assume two or more forms—*dimorphous, polymorphous;* but then each is characterized very definitely by special conditions of formation and existence.

When a compound crystallizes from the same solvent in different forms, it is only possible for the one to separate within definite ranges of temperature. The limit between these zones, the *temperature of transposition*, is theoretically expressed by the point of intersection of the solubility curves, belonging to the two crystalline forms. It is only the one or the other form that can appear under normal conditions above or below this temperature. From a supersaturated solution, and indeed a supersaturated solution of the two forms, it is possible artificially, by the introduction of one or the other form, to obtain each of the two kinds of crystals, and, indeed, both together. This is, however, only possible so long as the supersaturation continues. After that one of the two forms will gradually dissolve and that one will remain which is the more stable at the temperature of experiment.

The temperature of transposition varies for each solvent, and when impurities are present in the substances a greater or less variation in the temperature will occur, according to the degree of impurity. As regards the stability of the dimorphous modifications of one and the same substance, it may be said that this is naturally dependent upon the temperature. That form will be the more *unstable* which gives off heat and changes spontaneously into the other more *stable* modification. The cause of these differences may be traced to the fact that *chemical molecules identical in every respect orientate according to different laws, or unite to molecular aggregates* *of different magnitude.* Such modifications are *molecular isomerides*, the phenomenon being termed *molecular isomerism* (*physical isomerism*, Zincke, A. **182**, 244; O. Lehmann, Z. f. Kryst. **1**, 43, 97, 453).

Crystalline form bears some definite relation to the constitution of the carbon derivatives. At present it is true that we really know very little regarding this relation. That the slightest differences in chemical constitution find expression is demonstrated by the optically active carbon derivatives. Many optically active substances possess a hemihedral form, and the two optically active modifications of a carbon compound, although they exhibit the same geometrical constants, are distinguished by peculiar left and right types (enantiomorphous forms). They are not superposable. The difference between two optically active modifications, in which the atoms are similarly combined, is only due, according to the hypothesis of an *asymmetric* carbon atom (p. 45), to the difference in arrangement of the atoms within the molecule. From this it follows that this variation in arrangement finds expression in the crystalline form. (Compare, further, B. **29**, 1692.)

Laurent, Nicklès, de la Provostaye, Pasteur, Hjortdahl (see F. N. Hdw. **3**, 855) interested themselves in the determination of the influence that chemical relations of organic bodies exerted upon the geometrical properties of the crystals of the bodies under consideration. This problem, however, first appeared in the foreground of crystallographic study after P. Groth introduced the idea of morphotropy (Pogg, A. **141**, 31). By this term was understood the phenomenon of regular alteration of crystalline form produced by the entrance of a new atom or atomic group for hydrogen. Groth, Hintze, Bodewig, Arzruni, and others called frequent attention to such morphotropic relations particularly with the aromatic bodies (compare Physikal. Chemie der Krystalle von Andreas Arzruni, 1893).

The knowledge of the connection of crystalline form and chemical constitution is furthermore rendered difficult by the fact that as yet accurate determination of the magnitude of the crystal-molecule or crystal-element cannot be made. The possibility of doing this in the future may perhaps be found in van 't Hoff's theory of solid solutions.

So soon as the magnitude of the crystal molecule is known, we may expect a better insight into the relations existing between crystalline form and chemical constitution than has heretofore been possible. As to the rôle of water of crystallization in the salts of organic acids, consult Z. f. phys. Ch. **19**, 441.

2. SPECIFIC GRAVITY OR DENSITY.

By this term is understood the relation of the absolute weights of equal volumes of bodies, in which case we take as conventional units of comparison, water for solids and liquids, and air or hydrogen for gaseous bodies (see p. 27). The number representing the specific gravity of a compound is as great as that representing its density. It frequently occurs, therefore, that the terms specific gravity and density are used for each other.

Density of Gaseous Bodies.—For these, as we have already seen, the ratio of the specific gravity (gas density) to the chemical composition is very simple. Since, according to Avogadro's law, an equal number of molecules are present in equal volumes, the gas densities stand in the same ratio as the molecular weights. Being referred to hydrogen as unit, the gas densities are one-half the molecular weights. Therefore, the *specific volume*, *i. e.*, the quotient of the molecular weight and specific gravity, is a constant quantity for all gases (at like pressure and temperature).

Density of Liquid and Solid Carbon Derivatives.—In the solid and liquid states the molecules are considerably nearer each other than when in the gaseous condition. The size of the molecules and their distance from each other are unknown to us; the latter increases, too, with the temperature; therefore the theoretical groundwork for deduction of specific gravities is far removed from us. However, some regularities have been empirically established. These appear, upon comparing the specific volumes or molecular volumes, the quotients of the molecular weights and specific gravities.

The relations between the specific volumes of carbon compounds were first systematically studied by H. Kopp, in 1842 (A. **64**, 212; **92**, 1; **94**, 257; **96**, 153, etc., to **250**, 1). He felt justified from his observations in proposing: "That the specific volume of a liquid compound (molecular volume) at its boiling point is equal to the sum of the specific volumes of its constituents (of the atomic volumes), and that every element had a definite atomic volume in its compounds."

From this it would follow that: (1) Isomeric compounds possess approximately like specific volumes; (2) like differences in specific volumes correspond to like differences in composition.

The most recent researches,* based upon an abundance of material, and at the same time giving due consideration to the structural relations of the carbon compounds, prove conclusively that the supposed regularities, mentioned above, are unfounded. The fact is, isomeric compounds in no manner have equal molecular volumes, and their atomic volumes are not constant. The volume for the difference CH_2 is not constant in the different homologous series. The hydrogen volume varies (see A. **233**, 318; B. **20**, 767), as also that of oxygen (A. **233**, 322; B. **19**, 1594). For the molecular solution-volume, see Traube, A. **290**, 43; B. **28**, 2722.

Hence the molecular volumes in nowise represent the sums of the atomic volumes (the latter are scarcely determinable), and the specific gravities and molecular volumes depend less upon the volume of the atoms than upon their manner of linkage and upon the structure of the molecules. Therefore to deduce regularities in the specific volumes it is first necessary to carefully consider the chemical structure of the compounds. In this connection the influence of the double union of the C- atoms in the unsaturated compounds and the ring-form linking in the benzene derivatives, is significant. Assuming that the molecular volume of hydrogen is known,—that it equals 5.6,—it will be possible to calculate the molecular volume of an unsaturated olefine compound if the molecular volume of the corresponding saturated paraffin body is known. Thus, pentane $= 117.17$: therefore amylene $= 117.17 - 2 \times 5.6 = 105.97$. In fact, the molecular volume of amylene equals 109.95. Consequently $109.95 - 105.97 = 3.98$—the increase in molecular volumes caused by the double linkage in amylene (A. **220**, 298; **221**, 104; B. **19**, 1591; **20**, 779). The divalent union is therefore less intimate (pp. 38, 51) and the unsaturated compounds consequently show a greater heat of combustion (A. **220**, 321).

In the conversion of benzene hydrocarbons into their hexahydrides there is an increase in volume which is three times as great as in the conversion of the olefines into their corresponding paraffins. This would emphasize the theory that in the benzene nucleus there are three doubly combined carbon atoms. The specific gravities of the benzene hexahydrides is notably greater (consequently the molecular volumes are smaller) than their corresponding olefines, and that accounts for the fact

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* Lossen and others: A. **214**, 81, 138; **221**, 61; **224**, 56; **225**, 109; **233**, 249, 316; **243**, 1; R. Schiff, A. **220**, 71, 278; Horstmann, B. **19**, 1579; **20**, 766 and **21**, 2211.

that in the ring-linking of the C- atoms in the benzene nucleus there is an appreciable contraction in volume (A. **225**, 114 and B. **20**, 773). For further investigations relating to the benzene derivatives see Horstmann, B. **21**, 2211, and Neubeck, Z. phys. Chem., **1**, 649.

Schroeder determined the specific volumes of a number of solids (B. **10**, 848, 1871; **12**, 567, 1613; **14**, 21, 1607, etc.).

In determining the specific gravity of liquid compounds, a small bottle—a pyknometer (Landolt, p. 62, Anmerk. 2)—is used. Its contracted portion is provided with a mark. More complicated apparatus is employed where greater accuracy is sought (A. **203**, 4) (Fig. 6). Descriptions of modified pyknometers will be found in the Handwörterbuch v. Ladenburg, **3**, 238. A convenient form by Ostwald is described in J. pr. Ch. **16**, 396. To get comparable numbers, it is recommended to make all determinations at a temperature of 20° C., and refer these to water at 4°, and a vacuum. Letting m represent the weight of substance, v that of an equal volume of water at 20°, then the specific gravity at 20° referred to water at 4°, and a vacuum (with an accuracy of four decimals), may be ascertained by the following equation (A. **203**, 8):

$$d\frac{20}{4} = \frac{m \,.\, 099707}{v} + 0.0012.$$

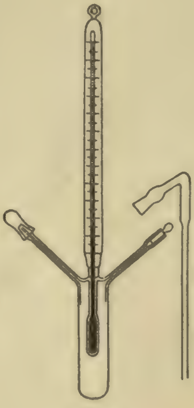

FIG. 6.

To find the specific volumes at the boiling temperature, the specific gravity at any temperature, the coefficient of expansion and the boiling point must be ascertained; with these data the specific gravity at the boiling point is calculated, and by dividing the molecular weight by this, there results the specific or molecular volume. Kopp's dilatometer (A. **94**, 257, compare Thorpe, J. Ch. S., **37**, 141, and Weger, A. **221**, 64) is employed in obtaining the expansion of liquids. For a method of getting the direct specific gravity at the boiling point, consult Ramsay, B. **12**, 1024; Schiff, A. **220**, 78, and B. **14**, 2761; also Schall, B. **17**, 2201, and Neubeck, Z. phys. Ch., **1**, 652.

3. MELTING POINT.

Every pure carbon compound, if at all fusible or volatile, exhibits a definite melting temperature. It is customary to determine this for the characterization of the substance, and to be assured of its purity. The melting point of a pure compound is not changed by recrystallization.

The slightest impurities frequently lower the melting point very considerably, whereas when foreign substances are present in larger amounts the melting point varies and is not well defined—*i. e.*, there is not a definite melting point. Pressure influences the fusion point in a very slight degree.

Determination of the Melting Point.—Such a determination is most accurately made by immersing the thermometer in a molten substance. However, this procedure would require large quantities of material (Landolt, B. **22**, R. 638).

Ordinarily, a small quantity of the finely pulverized material is introduced into a capillary tube, closed at one end, and this is attached to a thermometer by a thin platinum wire, or by adhesion through a drop of sulphuric acid; the thermometer and capillary tube are then raised somewhat. A beaker glass containing sulphuric acid or liquid paraffin is used to furnish the heat. A glass stirrer is moved up and down to equalize the temperature. A long-necked flask, containing sulphuric acid, is sometimes employed. In either case a test-tube is inserted or fused into the neck. In the latter case it is necessary that the flask should have a side-tubulure, as shown in Fig. 7 (B. **10**, 1800; **19**, 1971, Am. **5**, 337).

When the mercury thread of the thermometer extends far beyond the bath it is necessary, in accurate determinations, to introduce a correction. This is done by adding the value n(T—t) 0.000154 to the observed point of fusion; n is the length of the mercury column projecting beyond the bath expressed in degrees of the thermometer, T is the observed temperature, and t the temperature registered in the middle of the projecting portion of the mercury column. 0.000154 is the apparent coefficient of expansion of mercury in glass (B. **22**, 3072: Literatur und Tabellen). After the melting point has been approximately determined with an ordinary thermometer a more accurate determination may be made by introducing a shorter thermometer, divided into fifths, with a scale carrying a limited number of degrees (about 50°). See Fig. 7.

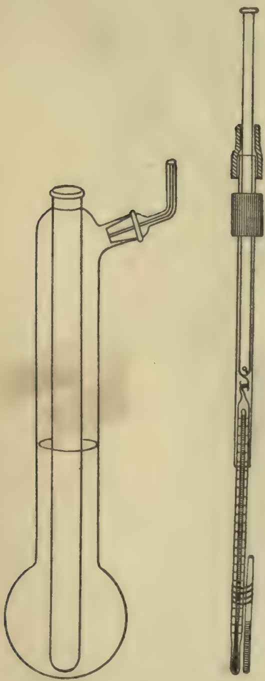

FIG. 7.

The melting points of the same compound, made by different observers, often accord more poorly than desirable for identification purposes. This is not so much due to the thermometers as to the manner in which the determination is made. By rapid heating the mercury of the thermometer will not have time to assume the fusion temperature. In the region of the melting point the heat must be moderated so that during the course of the fusion the thermometer rises *very* slowly. Far more concordant numbers might be obtained if a general use of short-scale thermometers were adopted and the *time* agreed upon for the mercury of the thermometer to rise through one degree of the scale during the observation of the fusion-process. For the determination of low melting points by means of the air thermometer, see B. **26**, 1052. For the determination of the melting points of organic bodies fusing at elevated temperatures, see B. **28**, 1629; at red-heat, B. **27**, 3129; of colored compounds, B. **8**, 687; **20**, 3290.

Regularities in melting points have not been especially noticed as yet. In the case of nucleus isomerides it has been observed that the member with the most branches generally shows the highest melting point (see butyl alcohols). Of the alkyl esters of the carboxylic acids those with the methyl residue have the highest melting points (see oxalic esters). In homologous series with like linkages the melting point alternately rises and falls (see saturated normal aliphatic mono- and dicarboxylic acids, B. **29**, R. 411). The members, having an uneven number of carbon atoms, have the lower melting points (Baeyer, B. **10**, 1286). This is also true of acid amides having from 6–14 carbon atoms (B. **27**, R. 551). The para-diderivatives of the isomeric benzene diderivatives usually melt at the highest points. In the case of the benzene nitro-compounds and their derivatives,—the azoxy-, azo-, hydrazo-, and amido bodies,—as well as the corresponding diphenyl-compounds, it has been observed that as oxygen is withdrawn the melting point rises until the azo-derivatives are reached, when it again descends until it meets the amido-bodies (G. Schultz, A. **207**, 362). For other regularities among the aromatic compounds consult B. **19**, R. 25; **27**, R. 558. For the melting points of mixtures, see B. **29**, R. 75.

4. BOILING POINT (DISTILLATION).

The boiling points of carbon derivatives, volatile without decomposition, are just as important for their characterization as the melting points. In case of the latter the influence of pressure is so slight that it is neglected, but the former vary very markedly by comparatively inappreciable changes in pressure. Hence in stating an accurate boiling point it is necessary to add the pressure at which it was observed. When the quantity of material is ample the boiling point is determined by distillation. For the determination of the boiling points of very small amounts of liquids see B. **24**, 2251, 944; **19**, 795; **14**, 88.

Distillation under Ordinary Pressure.—A boiling flask is used for this purpose. On the side of the neck is an exit tube. The neck of the flask is closed with a stopper, bearing a thermometer. It must not be forgotten that very frequently the vapors of organic substances attack ordinary corks or those of rubber, therefore the exit tube should be placed a considerable distance from the end of the neck. The mercury bulb of the thermometer is below the exit tube in the neck of the flask. The latter should be filled at least one-half with the liquid to be distilled.

If a thermometer is not wholly immersed in vapor, the external mercury column will not be heated the same as that on the interior, hence the recorded temperature will be less than the real. The necessary correction is the same as has already been given for the melting point. By using a shorter thermometer with scale not exceeding 50°, which can be wholly played upon by the vapor, the correction becomes unnecessary.

If the barometric column did not indicate a normal pressure of 760 mm. (B. **20**, 709) during the distillation, a second correction is necessitated. To avoid this correction it is advisable to reduce the pressure in the apparatus to the normal. The pressure regulators of Bunte (A. **168**, 139) and Lothar Meyer (A. **165**, 303) are adapted to this purpose.

*Distillation under Reduced Pressure.**—Attention has already been directed to the great variation in boiling points for variation in temperature. Many carbon derivatives whose decomposition temperature, at the ordinary pressure, is lower than their boiling points, can be boiled under reduced pressure at temperatures below the point at which they decompose. Distillation under reduced pressure is often the only means of purifying liquids which, at the ordinary pressure, boil with decomposition, and which cannot be crystallized. This method is of prime importance in scientific research in the laboratory. It is rapidly being introduced in technical operations with much success.

The introduction of boiling flasks with attached receivers (Fig. 8) has made the distillation, under diminished pressure, of bodies that readily congeal very convenient.

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*Compare Anschütz and Reitter: "Die Destillation unter vermindertem Druck im Laboratorium," 2. Aufl., 1895, Bonn. The tables in this book record the boiling points of over 400 inorganic and organic substances under reduced pressure. George W. Kahlbaum: "Siedetemperatur und Druck," Leipzig, 1885. "Dampfspannkraftsmessungen," Basel, 1893. Meyer Wildermann: "Die Siedetemperaturen der Körper sind eine Funktion ihrer chemischen Natur." B. **23**, 1254, 1468. W. Nernst und A. Hesse: "Siede- und Schmelzpunkte," Braunschweig, 1893.

The thermometer is introduced into a thin-walled tube drawn out into a capillary. The tube is closed with rubber tubing and a clip. A slow current of gas is drawn through the liquid during distillation, and in this way bumping is avoided. The distillation flask is best heated in a bath. To distil at pressures lying near the absolute vacuum, it will be found advantageous to use a Sprengel vacuum pump, which is set into motion according to Babo's method by the introduction of a water suction pump; compare Kahlbaum, B. **27**, 1386; F. Krafft and H. Weilandt, B. **29**, 1316; Precht, B. **29**, 1143.

It will be found that the apparatus described in the following references will answer for any desired pressure: Staedel, A. **195**, 218; B. **13**, 839. Schumann, B. **18**, 2085. For mercury thermometers registering temperatures from 550°–700° see B. **26**, 1815; **27**, 470.

Fractional Distillation.—Liquids having different boiling points are separated, when existing as mixtures, by *fractional distillation*—an operation that is performed in almost every distillation. Portions boiling between definite temperature intervals (from 1–10°, etc.) are caught apart and subjected to repeated distillation, the portions boiling alike being united. To attain a more rapid separation of the rising vapors, these should be passed through a vertical tube. In this the vapors of the higher boiling compound will be condensed and flow back, as in the apparatus employed in the rectification of spirit or benzene. To this end there is placed on the boiling flask a so-called *fractional* tube of Würtz. Excellent modifications of this have been described by Linnemann, Le Bel, Hempel and others. For the action of these boiling tubes see A. **224**, 259; B. **18**, R. **101**, and A. **247**, 3; B. **28**, R. 352, 938; **29**, R. 187.

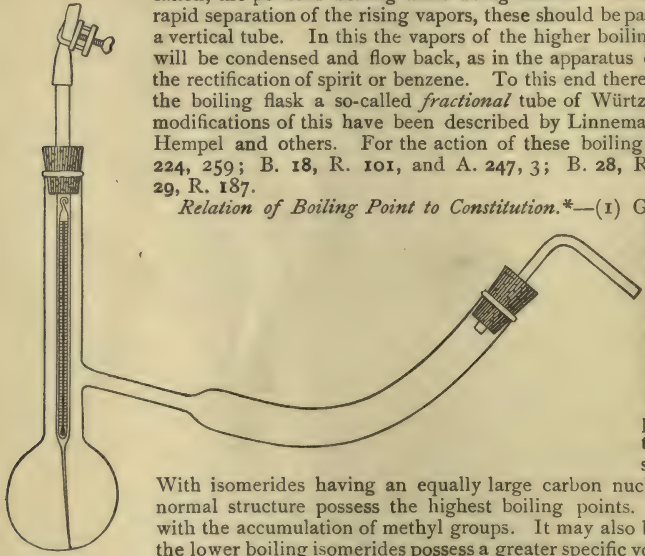

FIG. 8.

*Relation of Boiling Point to Constitution.**—(1) Generally the boiling point rises with the complication of the molecule. The unsaturated compounds boil at a higher temperature than those that are saturated. (2) With isomerides having an equally large carbon nucleus those of normal structure possess the highest boiling points. These fall with the accumulation of methyl groups. It may also be noted that the lower boiling isomerides possess a greater specific volume (B. **15**, 251). (3) The unsaturated compounds boil somewhat higher than the limit compounds.

The connection existing between the boiling points and chemical constitution of the compounds will be discussed later in the several homologous groups.

5. SOLUBILITY.

The hydrocarbons and their halogen substitution products are insoluble, or very slightly soluble, in water. They, however, dissolve very readily in alcohol and in ether, in which most other carbon derivatives are also soluble.

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* Compare W. Markwald: Ueber die Beziehung zwischen den Siedepunkten und der Zusammensetzung chemischer Verbindungen, welche bisher erkannt sind. Berlin.

Ether, but slightly miscible with water, is employed to extract many substances from these aqueous solutions, separatory funnels being used for this purpose.

The more oxygen a compound contains, the more readily soluble is it in water; especially is this true when several of the oxygen atoms are combined with hydrogen, *i. e.*, when hydroxyl groups are present in the organic compound.

The first members of homologous series of alcohols, aldehydes, ketones, and acids are soluble in water. As the carbon content increases, the hydrocarbon character, in relation to solubility, becomes more and more evident. The derivatives become more and more insoluble in water.

In addition to water, alcohol, and ether, other solvents employed with carbon derivatives are carbon disulphide, chloroform, carbon tetrachloride, methylal, acetone, glacial acetic acid, acetic ester, benzene, toluene, xylene, aniline, nitrobenzene, etc. Petroleum ether, derived from American petroleum, is especially valuable. It is composed of lower paraffins. It is often used to separate compounds from solvents with which it is miscible, because very many organic substances are insoluble or dissolve with difficulty in it.

The solubility of a carbon compound is dependent upon the temperature. It is constant for a definite temperature. This means is frequently employed for purposes of identification.

For the regularities of the solubilities of isomeric carbon derivatives, consult Carnelley, Phil. Mag. [6] **13**, 180; Carnelley and Thomson, J. ch. S. **53**, 801.

For apparatus in which to determine solubility, see V. Meyer, B. **8**, 998, and Köhler, Z. anal. Ch. **18**, 239.

6. OPTICAL PROPERTIES.

Color.—Most organic compounds are colorless, many are colored; thus, iodoform is yellow in color, while carbon tetraiodide is dark red. The presence of certain atomic groups is connected with definite colors; especially is this true of the aromatic derivatives. The nitro-bodies, for example, are more or less yellow in color, while the azo-derivatives vary from orange to red, etc., etc. (B. **27**, R. 20).

Dye-stuffs.—Many colored compounds, belonging almost exclusively to the aromatic series, can dye vegetable or animal fibers, either directly or through the agency of mordants. This property is of the greatest importance from a technical standpoint.

According to O. N. Witt an aromatic compound is a dye when it contains a chromophorous group, *e. g.*, NO_2, N_2, etc., and when, in addition, an acid or base group, *e. g.*, one or several OH, SO_3H, CO_2H and one or several NH_2 groups, enters the chromogen, *i. e*, a substance having a chromophorous group (B. **9**, 522).

a. **Refraction.**—The carbon compounds (like all transparent substances) possess a variable light refracting power.

The *coefficient of refraction*, the *refractive index* or *refractive quotient* (n) for homogeneous light passing from medium 1 into medium 2, represents the ratio of the propagating velocities v_1 and v_2 in both media; $n = \frac{v_1}{v_2}$. For single refracting media, in which similar optical deportment is observed in all directions (therefore not for the most crystals) n is independent of the direction of the incident light, so that if i and r are incident and refractive angles $n = \frac{v_1}{v_2} = \frac{\sin i}{\sin r}$, a constant number for light of a definite wave-length.

Specific Refractive Power or *Refraction Constant* (R).—The refraction index (n) varies with the temperature, consequently also with the specific gravity of the liquid. Their relation to each other is expressed by the equation : $R = \text{const.} = \frac{n^2 - 1}{(n^2 + 2)d_t}$ $\left(\text{or less accurate} = \frac{n - 1}{dt}\right)$[*] in which d_t is the sp. gr. of the liquid for the temperature t. It is an almost constant quantity for all temperatures, and is called the *specific refractive power* (B. **15**, 1031 ; **19**, 2761).

Molecular Refractive Power or *Molecular Refraction* MR is the specific refractive power multiplied by the molecular weight of a substance ; $M.R = \frac{(n^2 - 1)\,M}{(n^2 + 2)\,dt}$.

The molecular refraction of a liquid carbon compound is equal to the sum of the atomic refractions (mr, m′r′, m″r″) :

$$MR = amr + bm'r' + cm''r'',$$

in which a, b, c, represent the number of elementary atoms in the compound. The atomic refractions of the elements are deduced from the molecular refractions of the compounds obtained empirically, in the same manner as the atomic volumes are obtained from the molecular volumes. While it was formerly assumed that but *one* atomic refraction existed for each element in its compounds, later researches have proved that only the univalent elements have a constant atomic refraction, while that of the polyvalent elements, *e. g.*, oxygen, sulphur, carbon, is influenced by their manner of union.

The refraction is determined either for the yellow sodium line (D of the sun spectrum) or for the red hydrogen line H_α (C of the sun spectrum). "Singly linked" carbon has the atomic refraction (r_α) equal to 2.48 (A. **235**, 35 ; B. **22**, R. 224).

The double union ($C_2 =$) is 1.78 (for r_α), that of the triple union ($C_2 \equiv$) 2.18, *i. e.*, if two carbon atoms are "doubly linked," their atomic refraction equals $2 \times 2.48 + 1.78 = 6.74$, while in triple union it is $4.96 + 2.18 = 7.14$.

It is, therefore, obvious that important data relating to the manner of union of the atoms in the molecule of a carbon compound can be obtained from the molecular refractions (Landolt and Brühl). Thus the greater molecular refraction (by $3 \times 1.78 = 5.34$ units) of the benzene bodies, confirms the view previously deduced from chemical facts, that there are present in the benzene nucleus three "double-linked" carbon atoms (B. **20**, 2288 ; **24**, 666). However, the regularities noted above only hold good for bodies with slight dispersive power (the fatty bodies). In the case of substances possessing a greater dispersive power than cinnamyl alcohol, the molecular refraction is valueless for the determination of chemical structure (B. **19**, 2746 ; **24**, 1823).

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[*] See Landolt, Pogg. A. **123**, 595 ; B. **15**, 1031 ; Brühl, B. **19**, 2746 and 2821 ; A. **235**, **1**, and **236**, 233 ; B. **20**, 2288, and Z. phys. Ch. **1**, 307 ; Weegmann, Z. phys. Ch. **2**, 218 and 257 ; Ketteler, *ibid.*, **2**, 905 ; Eykmann, B. **29**, R. **584**.

The *reflectometer* of Pulfrich permits of a very rapid determination of the refractive power. It is more accurate and convenient in manipulation than a spectrometer.*

b. **Optical Rotatory Power,† Deviation of the Plane of Polarization by Liquid or Dissolved Carbon Compounds.**— Biot, in 1815, observed that many naturally occurring bodies were capable of rotating the plane of polarized light. These are the sugars, the terpenes, and camphors. He also showed, in 1817, how the vapors of turpentine deviate the plane of polarization, and concluded that this power was a property of chemical molecules. *Optically active carbon compounds* are those possessing the power of turning or rotating the plane of polarized light.

Specific Rotatory Power $[a]$.—The rotation (of the angle a) is proportional to the length l of the rotating plane (usually expressed in decimeters), hence the expression $\frac{a}{l}$ is a constant quantity. To compare substances of different density, in which very unequal masses fall upon the same plane, these must be referred to like density, and hence the rotation must be divided by the sp. gr. of the substance at a definite temperature. The expression $\frac{a}{l\,.\,d} = [a]_j$ or $[a]_D$, is called the *specific rotatory power* and is designated by $[a]_D$ or $[a]_j$, according as the rotation is referred to the yellow sodium line D or the transitional color j. For solid, active substances, with an indifferent solvent, the expression $[a] = \frac{100\ a}{p\,.\,l\,.\,d}$ will answer; in this, p represents the quantity of substance in 100 parts by weight of the solution, and d represents the specific gravity of the latter.

This specific rotatory power is constant for every substance at a definite temperature; it varies, however, with the latter, and is also influenced more or less by the nature and quantity of the solvent. Therefore, in the statement of the specific rotatory power of a substance, the temperature and the percentage amount of the solution must be included. By investigating a number of solutions of different concentration, the influence of the solvent may be established and the true specific rotation or the true rotatory constant of the pure substance, designated by A_D, may then be calculated. The product of the specific rotatory power and the molecular weight P divided by 100 is designated the *molecular rotatory power :*

$$[M] = \frac{P\,[a]}{100}.$$

Consult B. **21**, 191, 2586, 2599, upon the influence of inactive substances on the rotatory power.

The apparatus most suitable for the determination of rotation is fully described in the work of Landolt already referred to (see p. 62, note 2).

In 1848 Pasteur demonstrated that in optically active substances, such as tartaric acid and its salts, the rotatory power is mostly connected with the crystalline form, and is usually conditioned by the existence of hemihedral planes. In the discussion of the stereochemical or spacial theories reference was made to the fact that Pasteur considered the asymmetric structure of the molecules of optically active carbon compounds as the cause of their remarkable action upon polarized light.

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* C. Pulfrich, Das Totalreflectometer, etc., Leipzig, 1890.

† Compare Landolt, Das optische Drehungsvermögen, 1879.

According to the theory of Le Bel and van 't Hoff, the activity of the carbon compounds is dependent upon the presence of *asymmetric* carbon atoms (p. 45).

So far as they have been investigated, all optically active carbon compounds contain one or several asymmetric carbon atoms. However, many compounds containing asymmetric carbon atoms, when they exist as liquids, or when present in solution, have no effect upon polarized light. This is true when two molecules of opposite but equal rotatory power unite to a molecule of a physical, polymeric compound, *e. g.*, inactive lactic acid, inactive malic acid, inactive asparagine, inactive aspartic acid, racemic acid, etc.; also, when the half of a molecule neutralizes the rotation produced by the other half, as in mesotartaric acid. It has also been shown that in the conversion of optically active bodies into other derivatives the activity continues so long as the latter contain asymmetric carbon atoms. When the asymmetry disappears, the derivatives become inactive. The two active tartaric acids yield two active malic acids. Active asparagine yields active aspartic acid, active malic acid, etc., whereas the symmetrical succinic acid that may be obtained by reduction is inactive.

The conversion of optical antipodes into each other has been accomplished with the malic acids in the following manner:

Phosphorous pentachloride changes l-malic ester into d-chlorsuccinic ester, which silver oxide converts into d-malic acid. Conversely, d-malic ester and phosphorous pentachloride yield l-chlorsuccinic ester and the latter is then rearranged to l-malic acid (Walden, B. **29**, 138).

Thus far an optically active carbon derivative has not been indirectly prepared. The asymmetric bodies prepared artificially from inactive substances are inactive. This is explained by assuming that in such cases both modifications occur in equal amounts, and manifest a tendency to combine to the inactive, physically polymeric molecules.

Optically active carbon derivatives can be directly built up, because it is possible to decompose optically inactive asymmetric substances, whose molecule consists of a dextro- and lævo-molecule, into their components.

Breaking Down of Inactive Carbon Compounds into their Optically Active Components.—Methods **1**, **2**, and **4** were employed by Pasteur (1848) in his study of the racemates and racemic acid. This classic investigation of Pasteur contains the experimental basis for the theory of *stereochemistry* or the *space chemistry* of carbon (p. 45).

Method 1, based upon splitting by crystallization. The substance itself, or its derivatives with optically inactive compounds, is crystallized at varying temperatures and from various solvents. In the case under consideration it is possible to separate two substances showing enantiomorphous hemihedrism. Thus, from a solution of sodium ammonium racemate below 28° hemihedral crystals of sodium-ammonium dextro- and lævo-tartrates can be obtained (B. **19**, 2148).

Method 2, dependent upon the formation of compounds with optically active substances. Pasteur succeeded in separating d- and l-tartaric acids through their quinicine and cinchonine salts. This was because these, being no longer enantiomorphous, were distinguished by varying solubility, hence could be very easily separated from each other.

Ladenburg first used the latter method to resolve *inactive bases.* He did this by forming salts of the latter with an active acid. It was thus that he decomposed synthetic inactive conine (α-n-propylpiperidine) by means of dextrotartaric acid into its active components, and completed the synthesis of the first optically active vegetable alkaloid—conine—occurring in hemlock.

Method 3. Enzymes, such as maltase or emulsin, decompose racemic glucosides (E. Fischer, B. **28**, 1429).

Method 4. On introducing some suitable fungus such as *penicillium glaucum* into the aqueous solution of an inactive body, capable of decomposition, the one active modification will be destroyed by the growth of the fungus: thus, *racemic acid* yields *lævotartaric acid; inactive amyl alcohol* yields *dextroamyl alcohol; methyl propyl carbinol* yields lævo-methyl-propyl carbinol; *propylene glycol* yields lævo-propylene-glycol, etc.

In the case of the same optically inactive substance one fungus will leave the one modification unaltered, while another fungus will leave the other modification: thus, *Penicillium glaucum* or *Bacterium termo* will convert synthetic inactive mandelic acid into dextro-mandelic acid, while saccharomyces ellipsoideus or schizomycetes changes it to lævo-mandelic acid.

Consult B. **28**, 3000 for the complete literature relating to the decomposition of racemate modifications.

Carbon compounds, in which an asymmetric carbon atom is not present, could *not* be decomposed by these methods (A. **239**, 164; B. **18**, 1394).

Conversion of Optically Active Substances into their Optically Inactive Modifications.—While soluble salts of optically inactive, decomposable carbon compounds may be decomposed by crystallization under proper conditions of temperature, many others reunite to a salt of the inactive body, especially if the latter dissolves with difficulty. Solutions of lævo- and dextro-tartrate of calcium when mixed yield a precipitate of calcium tartrate, which dissolves with difficulty. The free, optically active modifications unite, as a rule, very easily, in solution and when mixed, to form the inactive decomposable modification, *e. g.*, lævo- and dextro-tartaric acid yield racemic acid. The esters of these acids conduct themselves in a similar manner: lævo- and dextro-tartaric methyl esters unite directly and in solution to racemic methyl ester (B. **18**, 1397). It is furthermore a fact that in energetic reactions, or when heated, the active varieties rapidly pass into the inactive forms, *e. g.*, dextro-tartaric at 175° yields racemic acid, and at 165° mesotartaric acid. At 180° dextro- and lævo-mandelic acids pass into inactive mandelic acid.

A corresponding deportment is observed in the decomposition of albuminoids, when heated with baryta, into inactive leucin, tyrosin, and glutamine, while at a lower temperature hydrochloric acid produces the active modifications (B. **18**, 388). For an experimental explanation of the transformation of optically active substances into their inactive modifications compare A. Werner in R. Meyer's Jahrbuch der Chemie 1, 130.

Philippe A. Guye has recorded observations upon the influence of the chemical constitution of carbon bodies upon the direction and change in their rotatory power. He especially considers the changes of *mass* in the different atoms and atomic groups in union with the asymmetric carbon atoms, and the consequent oscillations in the centres of gravity of the molecules: Étude sur la dissymétrie moléculaire: Arch. d. scienc. phys. et nat. [3] **26**, 97, Genève, 1891; compare Bull. soc. ch. 1896, 177.

c. **Magnetic Rotatory Power.**—Faraday, in 1846, discovered that transparent, isotropic, optically inactive bodies were capable of rotating the oscillating plane of polarized light when one column of the same was brought into the magnetic field or when it was surrounded by an electric current. The power of rotation only continued as long as these influences were active, hence this distinguished magnetic rotatory power from the rotatory power of optically active carbon compounds. It also varies with the location or position of the magnetic pole or the direction of the electric current.

Specific magnetic rotatory power is the degree of rotation the polarization plane of a ray of light sustains when it passes through a layer of liquid of definite thickness, exposed to the influence of a magnet. The unit of comparison is the rotation produced by a layer of water of like temperature and like thickness when exposed to the same magnetic field.

Molecular Magnetic Rotatory Power.—This is the degree of rotation produced by liquids where thickness has been so chosen that in each similar section there will be one molecular weight. The unit in this case can also be the molecular rotatory power of water.

W. H. Perkin, Sr., has occupied himself very extensively in deducing the relations of the magnetic rotatory power to the constitution of carbon derivatives. B. **17**, R. 549, contains an exhaustive article upon the magnetic rotatory power of 140 carbon compounds, as well as an account of the experiments.

7. ELECTRIC CONDUCTIVITY.

It is well known that substances capable of conducting electricity arrange themselves into two widely-separated groups: conductors of the first class, or those which conduct electricity without sustaining any change, and conductors of the second class, or those which constitute the electrolytes, and conduct only with their simultaneous separation into two *ions*. Conductivity can also be considered as a resistance, which the conductor opposes to the passage of the electricity. This resistance has the reciprocal value of the conductivity. The customary measure of conductivity or resistance is the mercury unit. This is a column of mercury of one sq. mm. cross section, and one meter in length, at the temperature 0°.

Ostwald's investigations have demonstrated that the conductivity of electrolytes is intimately related to chemical affinity. It is a direct measure of the chemical affinity of acids and bases. Therefore, the determination of the conductivity of electrolytes (in aqueous solution), to which all organic acids and their salts belong, is of great interest and importance for all carbon derivatives.

Kohlrausch * has suggested a very simple and accurate means of determining the conductivity of electrolytes, which has been extensively applied by Ostwald.†

It is dependent upon the application of alternating currents, produced by an induction spiral, so that the disturbing influence of galvanic polarization is obviated.

The conductivity of electrolytes is not referred to the percentage content of their aqueous solutions, but (as the conductivity is ascertained by the equivalent ions) to solutions containing a molecule, or an equivalent of substance in grams. This value is the *molecular* (or equivalent) conductivity of the substance (Z. phys. Ch. **2**, 567).

The strong acids have the greatest molecular conductivity, then the fixed alkalies and alkali salts. Most organic acids, on the contrary (*e. g.*, acetic acid), are poor conductors in a free condition, while their alkali salts approach those of the strong acids in conductivity. The *molecular* conductivity increases by about 2 per cent. per degree of temperature. It also increases with increasing dilution, and in the case of the poor conductors it is far more rapid than with the good conductors; in both instances it approximates a maximum (limiting) value. With good conductors this is attained at a dilution of 1000 litres to the gram-molecule; while with those poor in conducting power it is only reached when the dilution is indefinitely large. In fact, in such cases the conductivity is practically indeterminable.

An interesting observation in connection with the alkali salts of all acids is the variable increase of the molecular conductivity with increasing dilution. This is true both in the case of the strong and the weak acids (most organic acids belong to the latter class), and it varies according to their basicity. With sodium salts of monobasic acids, this increase equals from 10–13 units, by dilution of 32–1024 litres for the equivalent of substance, for the salts of dibasic acids from 20–25 units, for those of the tribasic 28–31, for those of the tetrabasic about 40, and those of the pentabasic about 50 units.

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* Wiedemann, A. **11**, 653.

† J. pr. Ch. **32**, 300, and **33**, 352; Z. phys. Ch. **2**, 561.

Thus it may be seen that the increase in conductivity of acids, in their sodium salts, offers a means of determining the basicity and, consequently, the molecular magnitude of acids (Ostwald, Z. phys. Ch. **1**, 74 and 97 ; **2**, 901 ; Walden, *ibid.*, **1**, 5.30, and **2**, 49).

Molecular conductivity has acquired still greater importance by its application to the measurement of the dissociation of the electrolytes; it is at the same time the measure of the reactivity or chemical affinity, first, of acids, then bases, and, finally, of salts.

Arrhenius's electrolytic dissociation theory maintains that in aqueous solution the electrolytes are more or less separated into their ions; this would give a simple explanation for the variations of solutions from the common laws (under osmotic pressure, under the depression at the freezing point, etc.). The dissociation is also manifest in the molecular conductivity, for the latter is dependent upon the degree of dissociation and the speed of migration of the free ions; it is directly proportional to the quantity of the latter.

Molecular conductivity increases with dilution and dissociation. When the latter is complete, it attains its maximum (μ_∞). The degree of dissociation (m) (or the fraction of the electrolyte split up into ions) for any dilution is found from the ratio of the molecular conductivity at this dilution (μ) to the maximum conductivity (for an indefinite dilution):

$$m = \frac{\mu}{\mu_\infty}.$$

The latter (μ_∞) cannot be directly measured in the case of free organic acids, because most of them are poor conductors. But it can be obtained from the molecular conductivity of their sodium salts, by deducting from their maximum values the speed of migration of the sodium-ions (41.1), and adding those of the hydrogen-ions (285.8).

Since the molecular conductivity depends upon the dissociation of the electrolytes into their ions, their alteration by dilution of solution must proceed by the same laws as those prevailing in the dissociation of gases. This influence of dilution or volume (v) upon the molecular conductivity, or the degree of dissociation (m) is, therefore, expressed in the equation:

$$\frac{m^2}{v(1-m)} = K,$$

which represents the law of dilution advanced by Ostwald (Z. phys. Ch. **2**, 36 and 270). This law has been fully confirmed by the perfect agreement of the calculated and observed values (van 't Hoff, Z. phys. Ch. **2**, 777).

The value, K, is the same at all dilutions for every monobasic acid; hence it is a characteristic value for each acid, and is the measure of its chemical affinity. The determination of these chemical affinity-constants by Ostwald for more than 240 acids, has proved that they are closely related to the structure and constitution of organic acids (Z. phys. Ch. **3**, 170, 241, 369). Literature: see Walden, Z. phys. Ch. **8**, 833. Affinity values of stereo-isomeric compounds: Hantzsch and Miolatti, B. **25**, R. 844.

Addendum: Determination of affinity-coefficients: Conrad, Hecht, and Brückner, Z. phys. Ch. **3**, 450; **4**, 273, 631; **5**, 289. Lellmann, B. **22**, 2101; A. **260**, 269; **263**, 286; **270**, 204, 208; **274**, 121, 141, 156. Nernst, R. Meyer's Jahrbuch **2**, 31.

HEAT OF COMBUSTION OF CARBON COMPOUNDS.*

"The quantity of heat evolved in any chemical change is a measure of the total work, both physical and chemical, occurring in it." The determination of the quantity of heat developed in complete combustion is alone adapted for the determination of the energy content of carbon compounds.

In determining the heat of combustion of a carbon compound Berthelot burned it in an atmosphere of oxygen, which was under a pressure of 25 atmospheres. The operation was conducted in calorimetric bombs lined on the interior with platinum or enamel. The electric spark was used to bring about the explosion, or the ignited combustion products, resulting from heating a thin iron wire by electricity, were made to serve the same purpose.

The method is so accurate that it answers for the detection of even traces of impurity in an organic compound, the heat of combustion of which is known (J. pr. Ch. N. F. **48,** 452; Z. f. angew. Ch., 1896, p. 486).

On the basis of Berthelot's principle: "The difference of the heats of combustion of two chemically equivalent systems is equal to the heat development which corresponds to the passage of the one system into the other," it is possible, knowing the heat of combustion of a carbon compound to calculate its heat of formation. The heat of combustion of the compound is deducted from the sum of the heats of combustion of its elements.

The heat of combustion of methane equals 21.9 cal.
" " " " " diamond-carbon is 94 cal., and
" " " " " hydrogen equals 69 cal.

As the complete combustion of methane proceeds according to the equation $CH_4 + 2O_2 = CO_2 + 2H_2O$, then the heat of formation of this hydrocarbon, at constant pressure, would be 20.1 cal.:

$$94 + 2 . 69 - 211.9 = 20.1.$$

The development of methods for the determination of the heats of combustion has engaged the attention of Favre and Silbermann, Thomsen, Stohmann, and particularly of Berthelot. In the last decade Stohmann especially determined the heat of combustion of numerous carbon derivatives, and published a tabulated account of the heats of combustion of organic bodies, made from 1852–1892, in the Z. f. phys. Ch. **6,** 334; **10,** 410.

The regularities thus far observed are as follows: With the hydrocarbons of the paraffin and olefine series the constant difference of CH_2 in composition corresponds to a constant increase of 158 cal. in the heat of combustion. Similar relations occur in other homologous series.

The heat of combustion of the two isomeric propyl alcohols is almost the same, consequently in the case of similar linking relations place-isomerism is without influ-

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* Practical introduction to thermochemical measurements by Berthelot, Grundriss der allg. Thermochemie, Plank, 1893. Die Grundsätze der Thermochemie, Hans Jahn, 2. Aufl. 1892. Grundriss der allg. Chemie, von Ostwald, 1889. Mecanique chimique, Berthelot, Paris, 1879.

ence upon the heat of formation and the heat of combustion. The difference of 6 cal. in the heats of combustion of fumaric acid (320.1 cal.) and maleïc acid (326.3 cal.) is more striking if we grant similar linking relations in the two acids, as is done by the adherents of the stereochemically different structural formulas of maleïc and fumaric acids (see these).

The passage from a double linkage to two single linkages, as well as a triple union to three simple unions is accompanied by considerable loss in energy. The relation of the heats of combustion of aromatic substances to their hydride derivatives is noteworthy. The differences of the heats of combustion of the dihydro- and their corresponding unaltered benzenes is considerably greater than the difference of the heats of combustion of the corresponding tetrahydro- and dihydro-, as well as the hexahydro- and tetrahydro-benzene derivatives. As to the contradictory conclusions which have been deduced from these facts in regard to the manner of union of the carbon atoms in the benzene ring, see A. **278**, 115; B. **27**, 1065; J. pr. Ch. N. F. **48**, 452; **49**, 453.

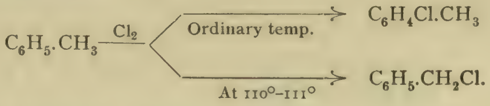
The varying stability of the tri-, tetra-, and penta-methylene rings referred by Baeyer to the varying ring-pressure (compare the introduction to the carbocyclic compounds), also manifests itself in the heats of combustion, whereas no difference could be detected between the penta- and hexa-methylene rings. As to how far observations upon the mentioned carbocyclic compounds can be applied to deductions upon constitution, it may be said, for example, that the heat of combustion of camphoric acid excludes the assumption of a tri- or tetra-methylene ring; however, it argues for the presence of a penta- or hexa-methylene ring in camphor (J. pr. Ch. N. F. **45**, 475; A. **292**, 125).

ACTION OF HEAT, LIGHT, AND ELECTRICITY UPON CARBON COMPOUNDS.

ACTION OF HEAT.

Substances that react most energetically upon each other do not do so at very low temperatures (Raoul Pictet, Arch. d. Scienc. phys. et nat. de Genève, 1893), even when subjected to the greatest pressure, and when their molecules are in most intimate contact. A definite temperature is essential for the occurrence of chemical action. The energy of a reaction, the time within which it proceeds, is largely dependent upon the temperature of the substances acting upon each other. Hence the determination of the most favorable temperature for the reaction is an important matter. It must be remembered that the heat developed in chemical changes frequently increases the initial reaction-temperature rapidly to the point of decomposition. In such cases the violence of the reaction must be moderated by cooling or by the use of indifferent diluents, in which the substances acting upon each other will be dissolved before the reaction occurs.

The action of chlorine upon toluene (see this) or upon methyl toluene shows particularly well how much the kind and nature of the action is dependent upon the temperature. At the ordinary temperature the chlorine substitutes the hydrogen of the phenyl residue, while at the boiling temperature it is the hydrogen of the methyl group which is replaced:



Numerous analogous observations are known.

In general, carbon compounds are much less stable under the influence of heat than the inorganic bodies. When the qualitative examination of organic bodies was discussed, mention was made that many carbon compounds decomposed with the separation of carbon under the influence of heat.

Other compounds, when heated at the ordinary temperature, rearrange themselves without alteration of their molecular magnitude, while some polymerize. Compounds, volatilizing undecomposed at ordinary pressure, decompose when their vapors are conducted through tubes heated to redness, and, as a rule, new bodies are formed together with partial carbonization. The splitting-off of hydrogen, the halogens, haloid acids, water and ammonia leads to a more intimate union of the already combined carbon atoms, and carbon atoms which previously were not united with one another not infrequently combine to yield carbocyclic and heterocyclic bodies. *Pyrocondensations* result (B. **11**, 1214).

In the special part of this volume such results from heat action will be so frequently encountered that it is not necessary to present examples of the special kinds of reactions at this time.

It may suffice to mention coal-tar; it contains the liquid bodies formed by the decomposition of coal under the influence of heat. This starting-out material is important both for the development of scientific, theoretical organic chemistry, as well as for technical chemistry (coal-tar industry). It is mainly composed of carbo- and heterocyclic compounds, stable under the influence of heat:

C_6H_6	$C_{10}H_8$	$C_{14}H_{10}$	
Benzene.	Naphthalene.	Anthracene, Phenanthrene.	
C_4H_4S	C_5H_5N	C_9H_7N	$C_{13}H_9N$
Thiophene.	Pyridine.	Quinoline and Isoquinoline.	Acridine.

2. ACTION OF LIGHT.

Light exerts a great influence upon carbon compounds. The well-known reactions of this kind in the field of inorganic chemistry have corresponding cases in the province of organic chemistry.

Light is able to bring about the decomposition, the rearrangement, and the synthesis of carbon bodies. Just as the haloid salts of silver decompose with silver deposition, so, too, the alkyl iodides separate iodine under the influence of light. Hence their colorless solutions gradually become yellow and finally dark brown in color.

Ethyl mercuric iodide breaks down into mercurous iodide and butane. Experience teaches that many other carbon derivatives decompose more or less rapidly when they are exposed to sunlight. Hence they must be preserved in the dark or in vessels constructed from brown colored glass, which absorbs the chemically active rays of sunlight. It is technically important that an organic dye should resist the influence of light. Most of them are not *fast* colors, they are, on the contrary, bleached by light.

Of the decomposition-reactions produced by sunlight mention may be made of the transposition shown by *succinic acid*, mixed with uranic oxide; it splits off carbon dioxide and propionic acid results (A. **133**, 253):

$$CO_2H.CH_2.CH_2.CO_2H = CO_2 + CH_3.CH_2.CO_2H.$$

Solutions of tartaric acid and citric acid, mixed with uranic oxide, are similarly decomposed by sunlight (A. **278**, 373).

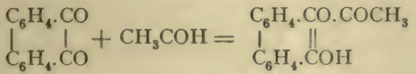
On exposing *anthracene* (see this) in benzene solution to sunlight it passes into a polymeric modification, *phenanthracene*.

The combination of *carbon monoxide* and chlorine, forming *carbonyl chloride* or *phosgene* (Davy) is analogous to the complete union of hydrogen and chlorine, forming hydrogen chloride, in sunlight:

$$H_2 + Cl_2 = 2HCl; \ CO + Cl_2 = COCl_2.$$

The action of chlorine upon marsh gas (p. 82), formaldehyde (B. **29**, R. 88), and other carbon derivatives which can be substituted is much influenced by sunlight.

The experiments conducted by Klinger show that the chemical action of sunlight is susceptible of more extended application than it has yet found, and that compounds can be produced by it, which could only be prepared in the ordinary chemical way by most powerful or refined means. He found that ethereal solutions of benzoquinone, benzil, and phenanthraquinone are reduced with the formation of aldehyde. Further, that acetaldehyde, isovaleraldehyde, and benzaldehyde unite, under the influence of sunlight, with phenanthraquinone in accordance with the equation:



$$\begin{array}{l} C_6H_4.CO \\ | \qquad | \\ C_6H_4.CO \end{array} + CH_3COH = \begin{array}{l} C_6H_4.CO.COCH_3 \\ | \qquad \| \\ C_6H_4.COH \end{array}$$

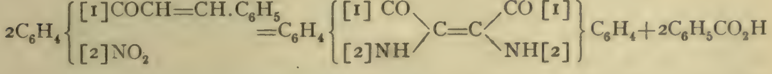
Phenanthraquinone. Acetaldehyde. Monacetyl phenanthrenhydroquinone.

Isovaleraldehyde and benzaldehyde also unite directly with benzoquinone, but in a still more striking manner, in that a *nucleus-synthesis* (p. 85) results. With benzaldehyde the reaction proceeds as follows:

$$C_6H_4O_2 + C_6H_5.COH = C_6H_5.CO.C_6H_3(OH)_2$$

Benzoquinone. Benzaldehyde. Dioxybenzophenone—isomeric with the expected Monobenzoyl hydroquinone.

o-Nitrobenzylidene acetophenone in ethereal solution is changed by sunlight to indigo and benzoic acid (Engler and Dorant, B. **28**, 2497):



The study of these reactions promises much for the interpretation of the chemical changes occurring in plants.

3. ACTION OF ELECTRICITY.

The actions of electricity upon organic bodies have not been well investigated. Some of the reactions induced by the aid of this agent possess great value for synthetic, organic chemistry. The only method which will cause the union of free hydrogen with free chlorine, consists in the action of the electric spark upon the two elements. Berthelot showed that carbon and hydrogen combined to acetylene on passing the electric spark over carbon points in an atmosphere of hydrogen: $2C + H_2 = CH \equiv CH$.

Fig. 9 represents the apparatus in which this important synthesis was carried out (A. chim. phys.; [4] **13**, 143; B. **23**, 1638).

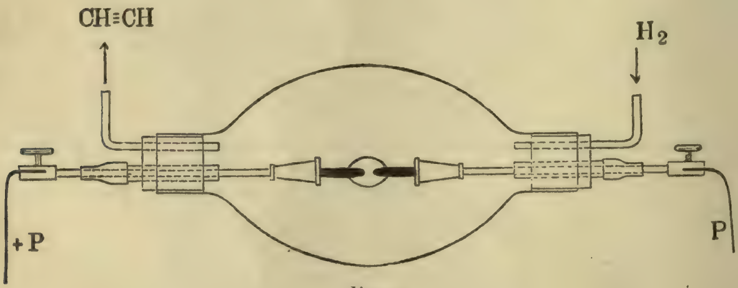


FIG. 9.

Acetylene and nitrogen (A. **150**, 60) under the influence of electric discharges, as well as cyanogen and hydrogen, unite to yield prussic acid (C. r. **76**, 1132), and carbon monoxide and hydrogen form methane (Brodie, A. **169**, 270).

$$\begin{matrix}CH\\ |||\\ CH\end{matrix} + N_2 = 2CNH; \quad \begin{matrix}CN\\ |\\ CN\end{matrix} + H_2 = 2CNH; \quad CO + 3H_2 = CH_4 + H_2O.$$

On the other hand, Kolbe decomposed the aqueous solutions of the potassium salts of monobasic carboxylic acids, especially potassium acetate, by the electric current, and thus prepared dimethyl or ethane. The following equation represents the breaking-down of the potassium acetate:

$$\overbrace{\begin{matrix}CH_3 \vdots CO_2\\ CH_3 \vdots CO_2\end{matrix}}^{+}\left|\overbrace{\begin{matrix}K & & HO\vdots H\\ K & + & HO\vdots H\end{matrix}}^{-}\right. = \overbrace{\begin{matrix}CH_3 & & CO_2\\ | & + & \\ CH_3 & & CO_2\end{matrix}}^{+} + \overbrace{\begin{matrix}KOH & & H\\ KOH & + & H\end{matrix}}^{-}$$

Kekulé applied this reaction to the saturated dicarboxylic acids, *e. g.*, succinic acid. Later he and Aarland used it with the unsaturated dicarboxylic acids: fumaric acid, maleïc acid, mesaconic acid, citraconic acid, and itaconic acid (A. **131**, 79; J. pr. Ch. [2] **6**, 256; **7**, 142), with the production of such unsaturated hydrocarbons as ethylene, acetylene, allylene. Kolbe and Moore obtained ethylene dicyanide from cyanacetic acid (B. **4**, 519). Crum Brown and J. Walker included the potassium salts of the acid esters of the dicarboxylic acids in the circle of these reactions, thus obtaining the neutral esters of dibasic acids, *e. g.*, potassium ethylmalonate yielded succinic diethyl ester (A. **261**, 107; B. **24**, R. 36; A. **274**, 41; B. **26**, R. 369, 380). In the electrolysis of an alcoholic solution of sodium malonic diethyl ester Mulliken obtained ethane tetracarboxylic ester (B. **28**, R. 450). For the electrolytic reduction of aromatic nitro-bodies consult B. **28**, 2349; **29**, 1390; see also p-amido-phenol.

CLASSIFICATION OF THE CARBON COMPOUNDS.

The chemical union of the carbon atoms and the character of the groups resulting from this is the basis of the division of the carbon derivatives into two principal classes: the **fatty** or **aliphatic** substances (from *ἄλειφαρ*, fat)—the *chain-like* or *acyclic carbon derivatives* or the *methane derivatives*, and the *cyclic compounds of carbon.*

The name of the first class is borrowed from the fats and fatty acids comprising it. These were the first derivatives accurately studied. It would be better to name them marsh gas or methane derivatives, inasmuch as they all can be obtained from methane, CH_4. They are further classified into saturated and unsaturated compounds. In the first of these, called also limit compounds or paraffins, the directly united quadrivalent carbon atoms are linked to each other by a single affinity. The number of n carbon atoms possessing affinities capable of further saturation, therefore, equals $2n + 2$ (see p. 38). Their general formula is C_nX_{2n+2}. Here X represents the affinities of the elements or groups directly combined with carbon. The unsaturated compounds result from the saturated by the exit of an even number of affinities in union with carbon. According to the number of affinities yet capable of saturation, the series are distinguished as C_nX_{2n}, C_nX_{2n-2}, etc.

The *methane derivatives* contain open carbon chains, the *cyclic derivatives* contain closed chains, or carbon rings. When carbon atoms alone have formed the ring, the resulting bodies are designated *carbo-cyclic compounds.*

The most important of these ring-shaped bodies is the ring containing six carbon atoms with six free valences.

All the *aromatic* or *benzene* compounds are derived from it. The importance of this group has gained for it a special position in the chemistry of carbon derivatives.

Compared with the aliphatic compounds they manifest such great differences in chemical deportment that they were formerly regarded as a second class of organic bodies, and as such were placed opposite to the first class or aliphatic substances.

With the advances in organic chemistry numerous compounds were being constantly discovered, which it is true contained ring-shaped carbon atoms, but in chemical deportment approached the fatty bodies more closely than the aromatic derivatives. In the so-called hydroaromatic compounds the more pairs of hydrogen atoms which attach themselves to the benzene nucleus in them, the greater will they resemble, in chemical character, the aliphatic derivatives. Even more closely allied to the latter are those substances which contain a ring consisting of three, four, or five carbon atoms—

the *trimethylene* derivatives,
tetramethylene derivatives,
pentamethylene derivatives.

These constitute the passage from the aliphatic bodies to the *hydroaromatic* compounds, to which the *aromatic* derivatives attach themselves.

There are many carbon compounds which contain "rings." In the formation of the latter not only carbon atoms, but also oxygen, sulphur, and nitrogen atoms have taken part.

Such bodies have been termed *heterocyclic compounds* (from ἕτερος, foreign). As a rule, these derivatives will be discussed at the conclusion of the remarks on the open chain bodies, from which they are derived by the exit of water, hydrogen sulphide, or ammonia, and to which they can again be changed. A large class of heterocyclic bodies, more especially *thiophene*, discovered by Victor Meyer, then the parent substances of the plant alkaloids—pyridine, quinoline, isoquinoline, etc., like the aromatic bodies, possess a very stable ring. It may be said in the case of many heterocyclic compounds that the substances with open chains from which they may be theoretically deduced do not really exist. Therefore such heterocyclic compounds will be purposely set to one side and be discussed after the carbo- and isocyclic derivatives. The divisions of the chemistry of the compounds of carbon would then be:

I. Fatty Bodies: *Aliphatic compounds, methane derivatives, chain-like or acyclic carbon derivatives.*

II. Carbocyclic Compounds.

III. Heterocyclic Compounds.

I. FATTY COMPOUNDS, ALIPHATIC SUBSTANCES OR METHANE DERIVATIVES, CHAIN-LIKE OR ACYCLIC CARBON DERIVATIVES.

I. HYDROCARBONS.

The hydrocarbons may be regarded as the parent substances from which all other carbon compounds arise by the replacement of the hydrogen atoms by different elements or groups.

The outlines of the linking of carbon atoms were presented in the introduction (p. 37). We distinguish, therefore, (1) *saturated* and (2) *unsaturated hydrocarbons*. The first only contain singly linked carbon atoms, while the unsaturated contain pairs of carbon atoms united doubly and trebly. As the first series has attained the limit of saturation by hydrogen, they are frequently called the *limit hydrocarbons*, or, after the first member of the series: marsh gas—the *methane hydrocarbons*. The limit hydrocarbons are not very reactive, but they are very stable; hence their designation as *paraffins* (from parum affinis).

A. Saturated or Limit Hydrocarbons, Paraffins, Alkanes, Marsh Gas or Methane Hydrocarbons, C_nH_{2n+2}.

Nomenclature and Isomerism.—In consequence of the equivalence (confirmed by facts) of the four affinities of carbon (see p. 37) no isomerides are possible for the first three members of the series C_nH_{2n+2}:

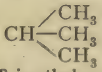
$$\underset{\text{Methane.}}{CH_4} \qquad \underset{\text{Ethane.}}{CH_3-CH_3} \qquad \underset{\text{Propane.}}{CH_3-CH_2-CH_3}$$

Formerly these hydrocarbons were designated the hydrides of univalent radicals—hydrocarbon residues or alkyls: methyl, ethyl, propyl, etc. Combined with the water residue or hydroxyl, they yielded the alcohols $C_nH_{2n+1}OH$. They were at first obtained from compounds of these radicals with other elements or groups; hence the names methyl hydride for methane, ethyl hydride for ethane, etc. The obtainable and first known derivatives of the alkyls C_nH_{2n+1} were their hydroxyl derivatives or the alcohols, *e. g.*, $C_2H_5.OH$, ethyl alcohol, and their halogen ethers. At the suggestion of A. W. Hofmann their names were formed later by replacing the final syllable "yl" of the alkyls by the final syllable "ane," so that methane was used for methyl, ethane for ethyl, propane for propyl, etc., and for the homologous series the name *alkanes* was adopted.

Two structural cases exist for the fourth member, C_4H_{10}:

$$\underset{\text{Normal Butane.}}{CH_3-CH_2-CH_2-CH_3}$$

and



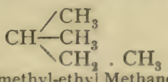
$$CH\begin{cases}CH_3\\CH_3\\CH_3\end{cases}$$

Trimethylmethane.
(Isobutane.)

In the name trimethylmethane for isobutane, isomeric with normal butane, is indicated that this substance is derived from methane by the replacement of three hydrogen atoms by three methyl groups.

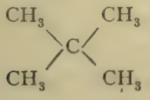
For the fifth member, pentane, C_5H_{12}, three isomerides are possible:

$$\underset{\text{Normal Pentane.}}{CH_3-CH_2-CH_2-CH_2-CH_3}$$



$$CH\begin{cases}CH_3\\CH_3\\CH_2\,.\,CH_3\end{cases}$$

Dimethyl-ethyl Methane. and

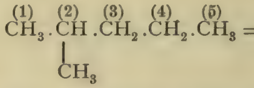


Tetramethyl Methane.

The number of theoretically possible isomerides now increases rapidly. Hexane, C_6H_{14}, has 6 isomerides; heptane, C_7H_{16}, 9 isomerides; octane, C_8H_{18}, 18 isomerides; tridecane, $C_{13}H_{28}$, 802 isomerides (B. **8**, 1056; B. **13**, 792).

Commencing with the fifth member, the names are formed from the Greek words representing numbers.

The "Geneva Commission" recommends the retention of the ending "ane," as first suggested by A. W. Hofmann (J. 1865, 413), for the hydrocarbons C_nH_{2n+2}. The hydrocarbons with branched carbon chains are considered alkyl substitution products of the normal hydrocarbons already contained in their formulas, and the carbon atoms of this normal hydrocarbon are numbered. The numbering is begun with that carbon atom to which the side-chain is adjacent:

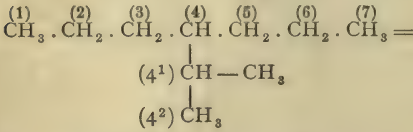


$$\overset{(1)}{CH_3}.\underset{\substack{|\\ CH_3}}{\overset{(2)}{CH}}.\overset{(3)}{CH_2}.\overset{(4)}{CH_2}.\overset{(5)}{CH_3} = [\text{Methyl-2-pentane}].$$

The carbon atoms of a longer substituting radical are also numbered, and, indeed, with two numbers. First, each atom is marked by the number indicating the place where the side-chain is attached to the normal chain; second, with particular numbers, beginning with the carbon atom joined to the central or main chain as number one.

Furthermore, should an alcohol radical attach itself to the middle carbon atom of the side-chain, then the expressions for the substituting radical are—

Metho-, etho-, etc., instead of methyl-, ethyl-, etc.:



$$\overset{(1)}{CH_3}.\overset{(2)}{CH_2}.\overset{(3)}{CH_2}.\underset{\substack{|\\ (4^1)\,CH-CH_3\\ |\\ (4^2)\,CH_3}}{\overset{(4)}{CH}}.\overset{(5)}{CH_2}.\overset{(6)}{CH_2}.\overset{(7)}{CH_3} = [\text{Metho-}4^1\text{-ethyl-4-heptane}].$$

The variation in structure of the carbon chain, or carbon nucleus, is the cause of isomerism in the paraffins. This type of isomerism is called chain- or nucleus-isomerism (p. 43).

Methods of Formation and Properties of the Paraffins.—The limit hydrocarbons are formed in the dry distillation of wood, turf, lignite, bituminous coal, and bog-head and cannel coal, rich in hydrogen; hence they are present in illuminating gas and in the light oils of coal-tar. They occur already formed in petroleum, particularly that from America, which consists almost exclusively of them, and contains all of them from methane to the highest. It is difficult to isolate the individual hydrocarbons from such mixtures. Before advancing to the general methods used in the preparation of the paraffins—methods by which the individual hydrocarbons can be easily obtained in pure condition—it will be best to discuss the two important members, *methane* and *ethane*.

(1) **Methane,** CH_4 (Methyl hydride), is produced in the decay of organic substances; therefore disengaged in swamps (marsh gas) and mines, in which, mixed with air, it forms fire-damp.

In certain regions, like Baku in the Caucasus and the petroleum districts of America, it escapes, in great quantities, from the earth. It is also present, in appreciable amount, in illuminating gas.

The synthesis of methane, the simplest hydrocarbon, from which all the fatty bodies may be derived, is particularly important. By the synthesis of a carbon derivative is understood its formation from the elements, or from such carbon derivatives which can be obtained from the elements. Under proper conditions hydrogen and carbon may be directly combined, with the production, however, of acetylene $CH \equiv CH$ (p. 76), and not methane. The latter can be obtained (1) from carbon disulphide CS_2 (which may be made directly from its constituents) if the vapors of this volatile substance, mixed with hydrogen sulphide gas, be passed over red-hot copper (Berthelot):

$$C + 2S = CS_2; \qquad CS_2 + 2H_2S + 8Cu = CH_4 + 4Cu_2S.$$

Or (2) the carbon disulphide is converted by chlorine into carbon tetrachloride CCl_4, and this reduced, by nascent hydrogen (sodium amalgam and water):

$$CS_2 + 3Cl_2 = CCl_4 + S_2Cl_2; \qquad CCl_4 + 8H = CH_4 + 4HCl.$$

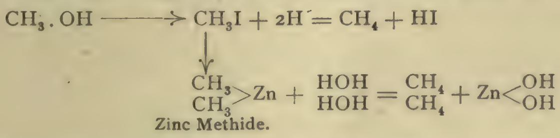
(3) Methane is also formed from carbon monoxide and hydrogen, if the mixture of gases be exposed in an induction tube to the action of electricity (p. 76, A. 169, 270):

$$2C + O_2 = 2CO; \qquad CO + 3H_2 = CH_4 + H_2O.$$

(4) Aluminium carbide is decomposed, in the cold, by water, forming methane and aluminium hydroxide (B. **27**, R. 620):

$$C_3Al_4 + 12H_2O = 2CH_4 + 2Al_2(OH)_6.$$

Methyl alcohol, or wood-spirit, $CH_3.OH$, can be converted into methane by first changing it to methyl iodide, and then (5) reducing the latter with nascent hydrogen (from moist zinc-copper), or with zinc dust in the presence of alcohol (B. 9, 1810); or (6) by preparing zinc methyl from methyl iodide and decomposing it with water:


$$\begin{array}{l} CH_3.OH \longrightarrow CH_3I + 2H = CH_4 + HI \\ \qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\qquad\quad \begin{matrix} CH_3 \\ CH_3 \end{matrix}{>}Zn + \begin{matrix} HOH \\ HOH \end{matrix} = \begin{matrix} CH_4 \\ CH_4 \end{matrix} + Zn{<}\begin{matrix} OH \\ OH \end{matrix} \end{array}$$

In the laboratory methane is made (7) by heating sodium acetate with soda lime. The active ingredient of the latter is sodium hydroxide. The addition of the lime is for the purpose of protecting the glass vessel from the corroding action of the molten sodium hydroxide:

$$CH_3.CO_2Na + NaOH = CH_4 + CO_3Na_2.$$

Methane is a colorless, odorless gas, compressible under great pressure and at a low temperature; its critical temperature is —82°, and its critical pressure 55 atm. It boils under 760 mm. pressure at —160° and at —164° its specific gravity is 0.415. Its density equals 8

($H = 1$) (or 0.5598, air $= 1$). It is slightly soluble in water, but more readily in alcohol. It burns with a faintly luminous, yellowish flame, and forms explosive mixtures with air, oxygen, and chlorine:

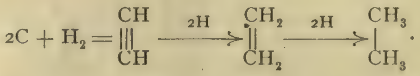
$$\underset{\text{1 vol.}}{CH_4} + \underset{\text{2 vols.}}{2O_2} = \underset{\text{1 vol.}}{CO_2} + \underset{\text{2 vols.}}{2H_2O} \text{ (steam).}$$

It is decomposed into carbon and hydrogen by the continued passage of the electric spark. When mixed with two volumes of chlorine it explodes in direct sunlight, carbon separating ($CH_4 + 2Cl_2 = C + 4HCl$); in diffused sunlight chlorine substitution products are produced:

$CH_4 + Cl_2 = HCl + CH_3Cl$—Monochlor-methane or methyl chloride.
$CH_3Cl + Cl_2 = HCl + CH_2Cl_2$—Dichlormethane or methylene chloride.
$CH_2Cl_2 + Cl_2 = HCl + CHCl_3$—Trichlormethane or chloroform.
$CHCl_3 + Cl_2 = HCl + CCl_4$—Tetrachlormethane or carbon tetrachloride.

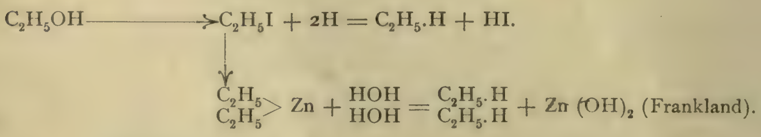
Methyl chloride renders possible the conversion of methane into methyl alcohol, ethane, ethyl alcohol, and acetic acid.

Ethane, *Ethyl Hydride, Dimethyl, Methyl Methane* $CH_3.CH_3$.—This hydrocarbon was discovered in 1848 by Frankland and Kolbe. It is formed (1) by the addition of hydrogen to the two unsaturated hydrocarbons, acetylene and ethylene, when the multiple linkage of the carbon atoms is broken down. It has been mentioned under methane that acetylene is produced by the direct union of carbon and hydrogen:



$$2C + H_2 = \begin{matrix} CH \\ ||| \\ CH \end{matrix} \xrightarrow{2H} \begin{matrix} CH_2 \\ || \\ CH_2 \end{matrix} \xrightarrow{2H} \begin{matrix} CH_3 \\ | \\ CH_3 \end{matrix}.$$

Ethane may be obtained from ethyl alcohol by means of (2) ethyl iodide or (3) by means of zinc ethyl, just as methane was prepared from methyl alcohol:



$$\begin{array}{lll} C_2H_5OH & \longrightarrow & C_2H_5I + 2H = C_2H_5.H + HI. \\ & & \downarrow \\ & & \begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix} > Zn + \begin{matrix} HOH \\ HOH \end{matrix} = \begin{matrix} C_2H_5.H \\ C_2H_5.H \end{matrix} + Zn(OH)_2 \text{ (Frankland).} \end{array}$$

Or (4) mercury ethide may be decomposed by concentrated sulphuric acid: $(C_2H_5)_2Hg + SO_4H_2 = 2C_2H_5.H + SO_4Hg$ (Schorlemmer). These last three methods led to the assumption that ethane was *ethyl hydride.* The following reactions show how ethane can be formed from the union of two methyl residues, and hence led to the view that the hydrocarbon was *dimethyl.* (5) Sodium is allowed to act upon methyl iodide, or (6) zinc methide may be substituted for the metal:

$$2CH_3I + 2Na = CH_3-CH_3 + 2\ NaI. \text{ (Würtz).}$$
$$2CH_3I + (CH_3)_2Zn = 2\ CH_3-CH_3 + ZnI_2.$$

A more convenient method (7) consists in heating acetic anhydride with barium dioxide:

$$2\,(C_2H_3O)_2O + BaO_2 = C_2H_6 + (C_2H_3O_2)_2Ba + 2CO_2.$$

From a theoretical point of view (8) the electrolysis of a concentrated solution of potassium acetate (p. 76) (the method used by Kolbe (1848) when he discovered ethane), is of great importance. The salt breaks down into potassium, its electro-positive constituent, appearing at the negative pole and separating hydrogen from water at that point, and also the unstable radical $CH_3.CO_2$—, which immediately decomposes at the electro-positive pole into —CH_3 and CO_2. Two methyl groups then unite to dimethyl, just as two hydrogen atoms combine to form a molecule of that element:

$$\begin{array}{c:c|cc:c} \multicolumn{2}{c|}{\overbrace{\hphantom{CH_3\quad CO_2}}^{+}} & \multicolumn{3}{c}{\overbrace{\hphantom{K\quad HO\quad H}}^{-}} \\ CH_3 & CO_2 & K & HO & H \\ & & + & & \\ CH_3 & CO_2 & K & HO & H \end{array} = \begin{array}{c}\overbrace{\hphantom{CH_3}}^{+}\\ CH_3\\ | \\ CH_3\end{array} + 2CO_2 + 2KOH + \begin{array}{c}\overbrace{\hphantom{H}}^{-}\\ H\\ |\\ H\end{array}$$

Both Kolbe and Frankland believed that ethyl hydride $C_2H_5.H$ differed from dimethyl $CH_3.CH_3$. Such a difference was not possible in the light of the valence theory. By converting the hydrocarbon from $(C_2H_5)_2Hg$ and that obtained in the electrolysis of potassium acetate into the same ethyl chloride Schorlemmer (1863) proved the identity of ethyl hydride $C_2H_5.H$ and dimethyl $CH_3.CH_3$, thus confirming a fundamental requirement of the valence theory:

$$(C_2H_5)_2Hg \xrightarrow{SO_4H_2} C_2H_5.H \xrightarrow{Cl_2} C_2H_5Cl.$$

$$2CH_3.CO\,OK \xrightarrow{\text{electric current}} CH_3.CH_3 \xrightarrow{Cl_2} CH_3CH_2Cl.$$

Ethane is a colorless and odorless gas. Its critical temperature equals + 34° and its critical pressure is 50.2 atmospheres. It boils at —93° under 760 mm. pressure. The specific gravity of liquid ethane at 0° is 0.466 (B. **27**, 3305). It acts like methane toward solvents.

Ethane can be converted into ethyl alcohol through its monochlor-substitution product.

Homologues of Methane and Ethane.—In preparing the homologous paraffins the homologues of ethyl alcohol $C_nH_{2n+1}.OH$ and the saturated fatty acids are used.

I. *Formation from compounds containing a like number of carbon atoms.*

(1) From the unsaturated hydrocarbons by the addition of hydrogen (see Ethane).

(2) By the reduction of alcohols, ketones, and carboxylic acids.

(a) The alcohols, for example ethyl alcohol, are first changed to chlorides, bromides, and iodides, and then reduced with nascent hydrogen, from zinc and hydrochloric acid, or from sodium amalgam and alcohol. The iodides can also be treated with aluminium chloride (B. **27**, 2766).

Thus propane has been prepared from the two propyl iodides, C_3H_7I, and trimethyl methane from the iodide of tertiary butyl alcohol by means of zinc and hydrochloric acid.

(b) The saturated fatty acids, $C_nH_{2n+1}.CO_2H$, particularly the higher members of the series, may be converted into the corresponding paraffins by heating them with concentrated hydriodic acid and red phosphorus to 200–250°:

$$\underset{\text{Stearic Acid.}}{C_{17}H_{35}.CO_2H} + 6HI = \underset{\text{Octadecane.}}{C_{18}H_{38}} + 3I_2 + 2H_2O.$$

(c) The ketones (see these), resulting from the distillation of the calcium salts of fatty acids, change to paraffins when they are heated with hydriodic acid. It is more practical to first prepare the keto-chlorides (p 102) by the action of phosphorus pentachloride upon the ketones, and then reduce these.

The last two reactions especially were applied (B. **15**, 1687, 1711; **19**, 2218) in the preparation of the normal hydrocarbons from nonane, $CH_3(CH_2)_7CH_3$, to tetracosane $CH_3(CH_2)_{22}CH_3$.

(3) Or, the alcohol is changed by an alkyl iodide into a zinc or mercury alkyl, and the zinc alkyls are then decomposed by water (see Methane and Ethane), and the mercury alkyls by acids (see Ethane).

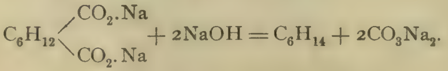
The iodides of the radicals may be heated with zinc and water, in sealed tubes, to 120–180°.

II. *Formation from compounds rich in carbon, by the splitting-off of carbon.*

(4) A mixture of the salts of fatty acids (the carboxyl derivatives of the alkyls) and sodium or potassium hydroxide is subjected to dry distillation (see Methane). Soda-lime is preferable to the last reagents.

When the higher fatty acids are subjected to this treatment the usual products are the ketones; hydrocarbons, however, are produced when sodium methylate is used (B. **22**, 2133).

The dibasic acids are similarly decomposed:



$$C_6H_{12}\begin{cases}CO_2.Na\\CO_2.Na\end{cases} + 2NaOH = C_6H_{14} + 2CO_3Na_2.$$

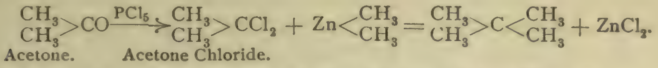
III. *Methods of Formation, consisting in the union of alkyls, previously not directly combined, with one another.*

(5) Method of Würtz: Action of sodium (or reduced silver or copper) upon the bromides or iodides of the alcohol radicals in ethereal solution (see Ethane). Thus with sodium:

C_2H_5I	yields $C_2H_5 . C_2H_5$	Diethyl or normal butane.
$CH_3CH_2CH_2I$	" $C_3H_7 . C_3H_7$	Dinormal propyl or normal hexane.
$CH_3CH_2CH_2CH_2I$	" $C_4H_9 . C_4H_9$	Dinormal butyl or normal octane.

This reaction proceeds especially easy with normal alkyl iodides having high molecular weights. Thus, Hell and Hägele, by fusing myricyl iodide with sodium, obtained *hexacontane*, $C_{60}H_{122}$, a compound having by far the longest normal carbon chain (B. **22**, 502). By using a mixture of the iodides of two primary alcohols hydrocarbons result from the union of different radicals. The iodides of optically active (p. 46) alcohols, *e. g.*, optically active amyl iodide, yield optically active paraffins (B. **27**, R. 852).

(6) Action of zinc alkyls upon alkylogens (see Ethane) and ketone chlorides. Thus, acetone chloride or β-dichlorpropane is changed by zinc methide into tetramethyl methane :



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CO \xrightarrow{PCl_5} \begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CCl_2 + Zn\!<\!\begin{matrix}CH_3\\CH_3\end{matrix} = \begin{matrix}CH_3\\CH_3\end{matrix}\!>\!C\!<\!\begin{matrix}CH_3\\CH_3\end{matrix} + ZnCl_2.$$

Acetone. Acetone Chloride.

(7) By the electrolysis of the alkali salts of fatty acids (see Ethane).

Synthetic Methods.—The last group of reactions comprises synthetic methods, serving for the building up of hydrocarbons. In the formation of methane from carbon disulphide and hydrogen sulphide it was explained what in general was understood by the synthesis of a carbon compound. Those reactions in which carbon atoms, not before combined with one another, are united claim particular importance in the synthesis of the compounds of carbon (Lieben, A. **146**, 200). Most of the carbon derivatives are due in the first place to the combining-power of the carbon atoms among themselves. Such reactions are the *synthetic methods of organic chemistry* in the more restricted sense. In the future we shall designate them *nucleus-syntheses*. They genetically bind together the members of an homologous series, and the homologous series among themselves, and carry the open carbon chains into closed chains or rings.

The *synthesis* of a carbon compound from derivatives of carbon of known structure is important for the recognition of its structure or constitution ; indeed, it is one of the most important aids.

Properties of the Paraffins.—The lowest members of the series up to butane and tetramethyl methane are gases at the ordinary temperature. The middle members are colorless liquids, with a faint but characteristic odor. The higher representatives, beginning with *hexadecane*, $C_{16}H_{34}$, melting at 18°, are crystalline solids. The highest members are only volatile without decomposition under reduced pressure. The boiling points rise with the molecular weights ; the difference for CH_2 is at first 30°, and with the higher members it varies from 25–13°.

The boiling points of *propane*, of the two *butanes*, the three *pentanes*, and the five known *hexanes* are given in the following table. All the theoretically possible isomerides are known :

		Structural Formula.	Boiling point below 760 mm.
C_3H_8	Propane	$CH_3.CH_2.CH_3$	—45°(B. **27**, 3306).
C_4H_{10}	Normal Butane	$CH_3.CH_2.CH_2.CH_3$	+ 1°(B. **27**, 2768).
	Trimethyl Methane	$CH_3.CH(CH_3)_2$	—17°
C_5H_{12}	Normal Pentane	$CH_3.(CH_2)_3.CH_3$	+ 38°
	Dimethyl-ethyl Methane	$CH_3.CH_2.CH(CH_3)_2$	+ 30°
	Tetramethyl Methane	$C(CH_3)_4$	+ 10°
C_6H_{14}	Normal Hexane	$CH_3(CH_2)_4CH_3$	+ 71°
	Methyl diethyl Methane	$CH_3(C_2H_5)_2CH$	+ 64°
	Dimethylpropyl Methane	$CH_3.CH_2.CH_2.CH(CH_3)_2$	+ 62°
	Di-isopropyl	$(CH_3)_2.CH.CH.(CH_3)_2$	+ 58°
	Trimethyl ethyl Methane	$CH_3.CH_2.C(CH_3)_3$	+ 43—48°

It is evident from this presentation that among isomerides those with normal structure (p. 42) have the highest boiling points. A general rule would be that with the accumulation of methyl groups in the molecule the boiling points of isomeric bodies are lowered. The same regularity will be again encountered in other homologous series. The subjoined table contains the melting points, boiling points, and the specific gravities of the known normal paraffins:

		Melting Point.		B. P.	Sp. Gr.	
Heptane,	C_7H_{16}	. . .		98.4°	0.7006(0°)	
Octane,	C_8H_{18}	. . .		125.5°	0.7188(0°)	
Nonane,	C_9H_{20}	—51°		149.5°	0.7330(0°)	
Decane,	$C_{10}H_{22}$	—32°	Under 760 mm. pressure.	173°	0.7456(0°)	
Undecane,	$C_{11}H_{24}$	—26.5°		194.5°	0.7745	at their m. p.
Dodecane,	$C_{12}H_{26}$	—12°		214°	0.773	
Tridecane,	$C_{13}H_{28}$	—6.2°		234°	0.775	
Tetradecane,	$C_{14}H_{30}$	+5.5°		252.5°	0.775	
Pentadecane,	$C_{15}H_{32}$	+10°		270.5°	0.775	
Hexadecane,	$C_{16}H_{34}$	+18°		287.5°	0.775	
Heptadecane,	$C_{17}H_{36}$	+22.5°		303°	0.776	
Octadecane,	$C_{18}H_{38}$	+28°		317°	0.776	
Nonadecane,	$C_{19}H_{40}$	+32°		330°	0.777	
Eicosane,	$C_{20}H_{42}$	+36.7°	Under 15 mm. pressure.	205°	0.777	
Heneicosane,	$C_{21}H_{44}$	+40.4°		215°	0.778	
Docosane,	$C_{22}H_{46}$	+44.4°		224.5°	0.778	
Tricosane,	$C_{23}H_{48}$	+47.7°		234°	0.778	
Tetracosane,	$C_{24}H_{50}$	+51.1°		243°	0.778	
Heptacosane,	$C_{27}H_{56}$	+59.5°		270°	0.779	
Hentriacontane,	$C_{31}H_{64}$	+68.1°		302°	0.780	
Dotriacontane,	$C_{32}H_{66}$	+70.0°		310°	0.781	
Pentatriacontane,	$C_{35}H_{72}$	+74.7°		331°	0.781	
Dimyricyl,	$C_{60}H_{122}$	+102°		. . .	. . .	

The limit hydrocarbons are insoluble in water. The lower and intermediate members are readily soluble in alcohol and ether. The solubility in these last two solvents falls with increasing molecular weight. Dimyricyl, $C_{60}H_{122}$, melting at 102°, is scarcely soluble in them.

The specific gravities of the liquid and solid hydrocarbons increase with their molecular weights, but are always less than that of water. It is remarkable that in the case of the higher members the specific gravities at the point of fusion are almost the same. They rise from 0.773 for dodecane, $C_{12}H_{26}$, to but 0.781 for pentatriacontane, $C_{35}H_{72}$; consequently the molecular volumes are nearly proportional to the molecular weights (B. **15**, 1719; A. **223**, 268).

The paraffins are not absorbed by bromine in the cold or sulphuric acid, being in this way readily distinguished and separated from the unsaturated hydrocarbons. They are not very reactive and are very stable, hence, their designation as *paraffins*. Fuming nitric acid and even chromic acid are without much effect upon them in the cold; when heated, however, they generally burn directly to carbon dioxide and water. Recently, n-hexane and n-octane have been nitrated by heating them with dilute nitric acid. When acted upon by chlorine or bromine they yield substitution products.

By means of the latter the paraffins can easily be converted, as observed under methane and ethane, into other derivatives.

Technical Preparation of the Limit Hydrocarbons.—The hydrocarbons, technically accessible, are applied in remarkably large quantities for illumination and heating purposes. They are also used as solvents for fats, oils, and resins, and as lubricants for machinery; finally, as salves.

The great abundance of *petroleum*, rock-oil (naphtha), is of the utmost importance to chemical industry. It is especially abundant in Pennsylvania and Canada, although it is also found in the Crimea along the Black Sea, and at Baku on the shore of the Caspian, as well as in Hungary, Galicia, Roumania, and the Argentine Republic. Its occurrence in Germany, in Hannover, and in Alsace is limited. Since the year 1859 efforts have been put forth to work oil wells, which have been known for many years, and also to make new borings. (See Höfer: Das Erdöl and seine Verwandten, 1888.)

The following data give some idea of the vast quantities in which this product is handled: In 1889 the yield of crude oil in America was about 35,000,000 barrels; in Russia, about 21,000,000 barrels; in other countries, 1,700,000 barrels, of which Alsace furnished 45,000 barrels and Hannover 6000 barrels. The barrel contains 159 liters. The consumption in Germany represented about 4,000,000 barrels (see F. Fischer, Hdb. d. ch. Technologie, 1893, S. 128).

In a crude state it is a thick, oily liquid, of brownish color, with greenish luster. Its more volatile constituents are lost upon exposure to the air; it then thickens and eventually passes into *asphaltum*. The greatest differences prevail in the various kinds of petroleum. It is very probable that petroleum has been produced by the distillation of the fatty constituents of fossil animals. This took place under great pressure and by the heat of the earth. The distillation of fish blubber under pressure has yielded products very similar to the American petroleum (Engler, B. **21**, 1816; **26**, 1449; Ochsenius, B. **24**, R. 594).

At the conclusion of his investigations on metallic carbides Moissan shows that on decomposing the metallic carbides in the interior of the earth with water hydrocarbons might arise, and these could cause the gas and petroleum wells (B. **29**, R. 614).

American petroleum consists almost exclusively of normal paraffins; yet minute quantities of some of the benzene hydrocarbons (cumene and mesitylene) appear to be present. In a crude form it has a specific gravity of 0.8–0.92, and distils over from 30–360° and beyond this. Various products, of technical value, have been obtained from it by fractional distillation: *Petroleum ether*, specific gravity 0.665–0.67, distilling about 50–60°, consists of pentane and hexane; *petroleum benzine*, not to be confounded with the benzene of coal tar, has a specific gravity of 0.68–0.72, distils at 70–90°, and is composed of hexane and heptane; *ligroïne*, boiling from 90°–120°, consists principally of heptane and octane; refined petroleum, called also kerosene, boils from 150–300° and has a specific gravity of 0.78–0.82. (For the apparatus of Engler and Abel intended to determine the flashing point of petroleum see Elsner: Die Praxis des Chemikers [1893] S. 399, 401; B. **29**, R. 553). The portions boiling at high temperatures are applied as lubricants; small amounts of vaseline and paraffins (see below) are obtained from them.

Caucasian petroleum (from Baku) has a higher specific gravity than the American; it contains far less of the light volatile constituents, and distils about 150°. Upward of 10 per cent. benzene hydrocarbons (C_6H_6 to cymene $C_{10}H_{14}$) may be extracted by shaking it with concentrated sulphuric acid; and in addition less saturated hydrocarbons, C_nH_{2n-8}, etc. (B. **19**, R. 672). These latter are also present in the German oils (Naphthenes, B. **20**, 595). That portion of the Caucasian petroleum insoluble in sulphuric acid consists almost exclusively of C_nH_{2n} hydrocarbons, the naphthenes, which belong to the cycloparaffins (p. 89), and are probably chiefly pentamethylenes, mixed, perhaps, with aromatic hydrides; hexahydroxylene=octonaphthene, hexahydromesitylene=non-naphthene (B. **16**, 1873; **18**, R. 186; **20**, 1850, R. 570). From its composition, Galician petroleum occupies a position intermediate between the American and that from Baku (A. **220**, 188).

German petroleum also contains benzene hydrocarbons (extracted by sulphuric acid), but consists chiefly of the saturated hydrocarbons and naphthenes (Kraemer, B. **20**, 595). The so-called petrolic acids are present in all varieties of petroleum, particularly that from Russia (Beilstein, Hdb. d. org. Ch., III Aufl., 522).

Products similar to those afforded by American petroleum are yielded by the tars resulting from the dry distillation of cannel coal (in Scotland) and a variety of coal found in Saxony. These tars contain appreciably greater quantities of unsaturated hydrocarbons associated with the naphthenes and paraffins, as well as the aromatic hydrocarbons present in the tar from bituminous shales (Heusler, B. **28**, 488; Z. f. anorg. Ch. 1896, S. 319). Large quantities of solid paraffins are also present in these tar oils.

By *paraffins*, we ordinarily understand the high-boiling (beyond 300°) solid hydrocarbons arising from the distillation of the tar obtained from turf, lignite, and bituminous shales. Paraffin was discovered by Reichenbach (1830) in the tar from beech-wood. They are more abundant in the petroleum from Baku than in that from America. Mineral wax, *ozokerite* (in Galicia and Roumania; also upon an island in the Caspian Sea, B. **16**, 1547) and *neftigil* (in Baku), are examples existing in a free, solid condition. For their purification the crude paraffins are treated with concentrated sulphuric acid, to destroy the resinous constituents, and then re-distilled. Ozokerite that has been directly bleached, without distillation, bears the name *ceresine*, and is used as a substitute for beeswax. Paraffins that liquefy readily and fuse between 30–40°, are known as *vaselines;* they find application as salves.

When pure, the paraffins form a white, translucent, leafy, crystalline mass, soluble in ether and hot alcohol. They melt between 45° and 70°, and are essentially a mixture of hydrocarbons boiling above 300°, but appear to contain also those of the formula C_nH_{2n}. Chemically, paraffin is extremely stable, and is not attacked by fuming nitric acid. Substitution products are formed when chlorine acts upon paraffin in a molten state.

B. Unsaturated Hydrocarbons.

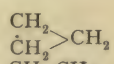
1. C_nH_{2n} : Olefines, Alkylens, Alkenes.
2. C_nH_{2n-2} : Acetylene Series.
3. C_nH_{2n-2} : Diolefine Series.
4. C_nH_{2n-4} : Olefinacetylene Series.
5. C_nH_{2n-6} : Diacetylene Series.

1. OLEFINES or ALKYLENS. C_nH_{2n}.

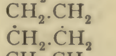
The hydrocarbons of this series contain two hydrogen atoms less than the limit hydrocarbons. All contain two adjacent carbon atoms united doubly to each other, or, as commonly expressed, they contain a double carbon linkage. The olefines readily add two univalent atoms or radicals; the double carbon union is then severed. Paraffins or their derivatives result.

The names of the olefines are derived from the names of the alcohols containing a like carbon content, with the addition of the suffix "ene": ethylene from ethyl, propylene from propyl, and finally for the series we have the name: *alkylens*. In the "Geneva names" the *yl* of the alcohol radicals is replaced by "ene": [ethene] from ethyl, [propene] from propyl, and for the series: *alkenes*. In long series the position of the double union is indicated by an added number (p. 80). Methylene, $=CH_2$, the hydrogen compound corresponding to CO, has thus far resisted isolation as completely as $—CH_3$. Two $=CH_2$ groups invariably unite to ethylene—the first member of the series. Beginning with the second member of the series we find, as we advance, that the olefines have isomerides in the ring-shaped hydrocarbons—the **cycloparaffins** or **cyclic limit hydrocarbons**:

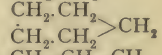
Propylene has an isomeride in *trimethylene*—Cyclopropane


$$\begin{array}{l}CH_2 \\ \dot{C}H_2\end{array}\!>\!CH_2$$

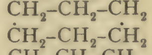
The three butylenes have an isomeride in *tetramethylene*— Cyclobutane


$$\begin{array}{l}\dot{C}H_2.\dot{C}H_2 \\ \dot{C}H_2.\dot{C}H_2\end{array}$$

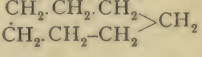
The five amylenes " " " " *pentamethylene*— Cyclopentane


$$\begin{array}{l}CH_2.CH_2 \\ \dot{C}H_2.CH_2\end{array}\!>\!CH_2$$

The hexylenes are isomeric with *hexamethylene*— [Cyclohexane] hexahydrobenzene


$$\begin{array}{l}\dot{C}H_2–CH_2–\dot{C}H_2 \\ \dot{C}H_2–CH_2–\dot{C}H_2\end{array}$$

The heptylenes are isomeric with *suberene*—heptamethylene [Cycloheptane]


$$\begin{array}{l}CH_2.CH_2.CH_2 \\ \dot{C}H_2.CH_2–CH_2\end{array}\!>\!CH_2$$

The cycloparaffins are more closely allied, in chemical character, to the paraffins than to their isomeric olefines, as they only contain singly linked carbon atoms. They lack in additive power, as the addition of hydrogen could only result in a rupture of the ring. In their derivatives, the cycloparaffins form the transition from fatty bodies to the aromatic compounds. They will not be considered in the discussion of the olefines.

Olefine isomerides appear first with butylene. Three modifications are possible and are also known:

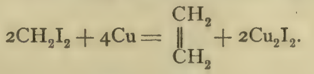
(1) $CH_3—CH_2—CH=CH_2$ Butylene [Butene 1]. (2) $CH_3—CH=CH—CH_3$ Pseudobutylene [Butene 2]. (3) $CH_2=C(CH_3)_2$ Isobutylene [Methyl Propene].

Five olefines of the formula C_5H_{10} are possible, etc.

Ethylene is the type of olefines. It will now receive attention.

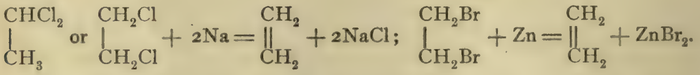
Ethylene, $CH_2=CH_2$ [*Ethene*], *Elayl;* called *oil-forming gas* because, by the action of chlorine, it yields an oily compound, ethylene chloride (see this). This property has given the name to this homologous series. Ethylene is formed in the dry distillation of many organic bodies, and is, therefore, present in illuminating gas (4 to 5 per cent.).

Methods of Formation.—(1) By heating methylene iodide, CH_2I_2, with metallic copper to 100° in a sealed tube (Butlerow):



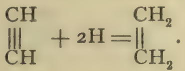
$$2CH_2I_2 + 4Cu = \begin{array}{l}CH_2\\ \|\\ CH_2\end{array} + 2Cu_2I_2.$$

(2) By the action of metallic sodium upon ethylidene chloride (Tollens) and ethylene chloride, as well as from zinc and ethylene bromide:



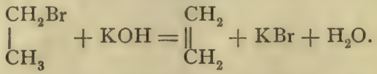
$$\begin{array}{l}CHCl_2\\ |\\ CH_3\end{array} \text{ or } \begin{array}{l}CH_2Cl\\ |\\ CH_2Cl\end{array} + 2Na = \begin{array}{l}CH_2\\ \|\\ CH_2\end{array} + 2NaCl; \quad \begin{array}{l}CH_2Br\\ |\\ CH_2Br\end{array} + Zn = \begin{array}{l}CH_2\\ \|\\ CH_2\end{array} + ZnBr_2.$$

(3) By the action of zinc and ammonia upon copper acetylide:



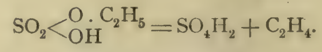
$$\begin{array}{l}CH\\ |||\\ CH\end{array} + 2H = \begin{array}{l}CH_2\\ \|\\ CH_2\end{array}.$$

(4) When alcoholic potash acts upon ethyl bromide:



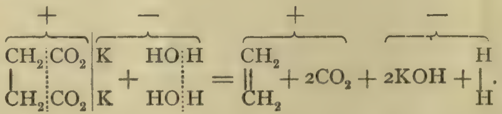
$$\begin{array}{l}CH_2Br\\ |\\ CH_3\end{array} + KOH = \begin{array}{l}CH_2\\ \|\\ CH_2\end{array} + KBr + H_2O.$$

(5) Upon heating ethyl sulphuric acid (see below). This is the method usually pursued in the laboratory for the preparation of ethylene (A. **192**, 244):



$$SO_2{<}\begin{array}{l}O\,.\,C_2H_5\\ OH\end{array} = SO_4H_2 + C_2H_4.$$

(6) Electrolyze a concentrated solution of potassium succinate (see ethane) (Kekulé):

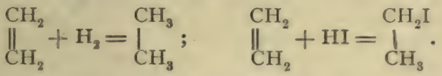


$$\overbrace{\begin{array}{l}CH_2 \vdots CO_2\\ |\\ CH_2 \vdots CO_2\end{array}}^{+} \Bigg| \overbrace{\begin{array}{l}K \quad HO \vdots H\\ \quad + \\ K \quad HO \vdots H\end{array}}^{-} = \overbrace{\begin{array}{l}CH_2\\ \|\\ CH_2\end{array}}^{+} + 2CO_2 + \overbrace{2KOH + \begin{array}{l}H\\ |\\ H\end{array}}^{-}.$$

Ethylene is a colorless gas, with a peculiar, sweetish odor. Water dissolves but small quantities of it, while alcohol and ether absorb about 2 volumes. It is liquefied at 0°, and a pressure of 42 atmospheres. Its critical temperature is 13°, while its critical pressure exceeds 60 atmospheres. It melts at — 169°, and at ordinary pressure boils at — 105°, and is suitable for the production of very low temperatures. It burns with a bright, luminous flame, decomposing into methane and acetylene (B. **27**, R. 459). In chlorine gas the flame is very smoky; a mixture of ethylene and chlorine burns away slowly when ignited. It forms a very explosive mixture with oxygen (3 volumes).

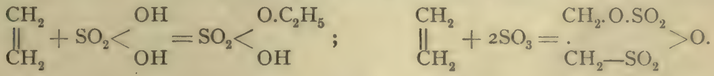
(1) Aided by platinum black it will combine with hydrogen at ordinary temperatures, yielding C_2H_6 (B. **7**, 354).

(2) It is absorbed by concentrated hydrobromic and hydriodic acids at 100°, with the production of C_2H_5Br and C_2H_5I:



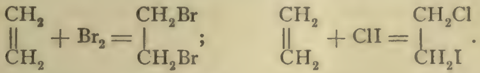
$$\begin{array}{c}CH_2\\ \|\\ CH_2\end{array} + H_2 = \begin{array}{c}CH_3\\ |\\ CH_3\end{array};\qquad \begin{array}{c}CH_2\\ \|\\ CH_2\end{array} + HI = \begin{array}{c}CH_2I\\ |\\ CH_3\end{array}.$$

(3) It combines with sulphuric acid at 160–174°, forming ethyl sulphuric acid; and with sulphuric anhydride it yields carbyl sulphate:



$$\begin{array}{c}CH_2\\ \|\\ CH_2\end{array} + SO_2{<}\begin{array}{l}OH\\ \\ OH\end{array} = SO_2{<}\begin{array}{l}O.C_2H_5\\ \\ OH\end{array};\qquad \begin{array}{c}CH_2\\ \|\\ CH_2\end{array} + 2SO_3 = \begin{array}{l}CH_2.O.SO_2\\ \\ CH_2—SO_2\end{array}{>}O.$$

(4) It unites readily with chlorine and bromine, as well as with alcoholic iodine, and the two modifications of iodine chloride:



$$\begin{array}{c}CH_2\\ \|\\ CH_2\end{array} + Br_2 = \begin{array}{c}CH_2Br\\ |\\ CH_2Br\end{array};\qquad \begin{array}{c}CH_2\\ \|\\ CH_2\end{array} + ClI = \begin{array}{c}CH_2Cl\\ |\\ CH_2I\end{array}.$$

(5) It forms the monochlorhydrin of glycol by its union with hypochlorous acid.

(6) Ethylene glycol itself, however, is produced by carefully oxidizing ethylene with dilute potassium permanganate, which acts as if hydrogen peroxide added itself to the ethylene:

$$\begin{array}{c}CH_2\\ \|\\ CH_2\end{array} + ClOH = \begin{array}{c}CH_2Cl\\ |\\ CH_2OH\end{array};\qquad \begin{array}{c}CH_2\\ \|\\ CH_2\end{array} + \begin{array}{c}OH\\ |\\ OH\end{array} = \begin{array}{c}CH_2OH\\ |\\ CH_2OH\end{array}.$$

Ethylene Homologues.—Higher olefines are found in the tar from bituminous shales (B. **28**, 496). Just as ethyl alcohol is the most suitable substance for the preparation of ethylene, so are its homologues the best starting-out material for the production of the homologues of ethylene.

Methods of Formation.—(1) The halogen derivatives, readily formed from the alcohols, are digested with alcoholic sodium or potassium hydroxide.

In this reaction the haloid (especially the iodides) derivatives corresponding to the secondary and tertiary alcohols break up very readily. *Propylene* has been obtained from isopropyl iodide, *a-butylene* from the iodide of normal butyl alcohol, *β-butylene* from secondary butyl iodide, and *isobutylene* from the iodide of tertiary butyl alcohol. Many others have been prepared in the same way. Heating with lead oxide effects the same result (B. **11**, 414). Tertiary iodides yield olefines when treated with ammonia.

(2) Distil the monohydric alcohols, $C_nH_{2n+1}OH$, with dehydrating agents, *e. g.*, sulphuric acid, chloride of zinc, and phosphorus or boron trioxide. These remove one molecule of water. Isomeric and polymeric forms are produced along with the normal olefines.

The secondary and tertiary alcohols decompose with special readiness. The higher alcohols, not volatile without decomposition, suffer the above change when heat is applied to them; thus cetene, $C_{16}H_{32}$, is formed on distilling cetyl alcohol, $C_{16}H_{34}O$.

When sulphuric acid acts upon the alcohols, acid esters of sulphuric acid (the so-called acid ethereal salts—see these) appear as intermediate products. When heated these break down into sulphuric acid and $C_n H_{2n}$ hydrocarbons (compare ethylene).

The higher olefines may be obtained from the corresponding alcohols by distilling the esters they form with the fatty acids. The products are an olefine and an acid (B. **16**, 3018):

$$\underset{\text{Dodecyl Ether of Palmitic Acid.}}{C_{16}H_{31}O.O.C_{12}H_{25}} = \underset{\text{Palmitic Acid.}}{C_{16}H_{31}O.OH} + \underset{\text{Dodecylene.}}{C_{12}H_{24}}.$$

(3) By the action of metals upon the halogen addition products of the olefines (see ethylene).

(4) Electrolyze the potassium salts of saturated dicarboxylic acids (see ethylene).

(5) When zinc alkylens act upon brom-olefines, *e. g.*, $CH_2=CHBr$, which with zinc yields α-butylene or ethyl ethylene.

(6) Olefines have also been obtained by the reaction of Würtz (p. 84).

(7) The formation of higher alkylens in the action of lower members with tertiary alcohols or alkyl-iodides is noteworthy. Thus, from tertiary butyl alcohol and isobutylene, with the assistance of zinc chloride or sulphuric acid, we get isodibutylene (A. **189**, 65; B. **27**, R. 626):

$$(CH_3)_3C.OH + CH_2 : C(CH_3)_2 = \underset{\text{Isodibutylene.}}{(CH_3)_3C.CH : C(CH_3)_2} + H_2O.$$

The action of the $ZnCl_2$ is due to the formation of addition products, *e. g.*, trimethyl ethylene and zinc chloride unite to the crystalline compound $(CH_3)_2C = CHCH_3,2ZnCl_2$. Water converts this into dimethyl-ethyl carbinol, while hydrogen chloride produces the chloride of the latter. This chloride and trimethyl ethylene then unite to a saturated chloride, which on distillation splits off hydrochloric acid and yields diamylene (B. **25**, R. 865).

Tetramethyl ethylene (B. **16**, 398) is produced on heating β-isoamylene (see p. 94) with methyl iodide and lead oxide:

$$(CH_3)_2C : CH.CH_3 + CH_3I = (CH_3)_2C : C(CH_3)_2 + HI.$$

In the dry distillation of many complicated carbon compounds the olefines are produced along with the normal paraffins, hence their presence in illuminating gas and in tar oils.

Properties and Rearrangements of the Olefines.—So far as physical properties are concerned, the olefines resemble the normal hydrocarbons; the lower members are gases, the intermediate ethereal liquids, while the higher (from $C_{16}H_{32}$ up) are solids. Generally their boiling points are a few degrees higher than those of the corresponding paraffins.

In chemical properties, on the other hand, they differ greatly from the paraffins.

Being unsaturated, they can unite directly with two univalent atoms or groups; then the double binding becomes single.

They combine:

(1) With nascent hydrogen, forming paraffins with a like number of carbon atoms (see ethylene).

(2) With HBr and with especial readiness with HI.

The haloid acids attach themselves in such a manner to the mono- and di-alkyl ethylenes that the halogen unites with the carbon atom holding the fewest hydrogen atoms. As such alkylized ethylenes can be prepared from the proper primary alcohols by the splitting-off of water, such reactions can be employed to convert primary into secondary alcohols, and also tertiary alcohols (p. 110).

The olefines are also capable of combining with the fat-acids (B. 25, R. 463) when exposed to a high heat (290–300°), *e. g.*:

$$\underset{\text{Pentyl-ethylene.}}{C_5H_{11}CH = CH_2} + CH_3.CO_2H = \underset{\text{Sec. Heptyl Acetate.}}{C_5H_{11}CH(O.CO.CH_3).CH_3}.$$

(3) Concentrated sulphuric acid absorbs them, forming ethereal salts. This is a reaction which can be used to change olefines into alcohols and also to separate them from paraffins (see p. 90).

(4) They form dihaloids (see ethylene) with Cl_2, Br_2, I_2, ClI. These can be viewed as the haloid esters of the dihydric alcohols—the glycols, into which they can be converted.

(5) They yield so-called chlorhydrins with aqueous hypochlorous acid. These are the basic esters of the glycols (see ethylene).

(6) Energetic oxidation severs the double union of the olefines. Potassium permanganate in dilute solution changes them to glycols (B. 21, 1230, 3359).

The last three reactions afford a means of converting monacid (monohydric) alcohols into dihydric alcohols or glycols (see these). The olefines form the part of aids in these changes, *e. g.*:

(7) N_2O_3 and N_2O_4 convert the olefines into *nitrosites* and *nitrosates* (see these). They are the nitrites and nitrates of oximes of oxyaldehydes and oxyketones. The olefines can even take up nitrosylchloride (B. 12, 169; 27, 455, R. 467). The resulting addition products are changed by boiling water, alcoholic potash, and ammonia back into the olefines (B. 29, 1550).

(8) *Polymerization of Olefines.*—When acted upon by dilute sulphuric acid (B. 29, 1550), zinc chloride, boron fluoride, and other substances, many olefines sustain, even at ordinary temperatures, a polymerization, in consequence of the union of several molecules. Thus there result from isoamylene, C_5H_{10}: di-isoamylene, $C_{10}H_{20}$; tri-isoamylene, $C_{15}H_{30}$, etc. Butylene and propylene behave in the same way. Ethylene, on the other hand, is neither condensed by sulphuric acid nor by boron fluoride.

The polymerides act like unsaturated compounds, and contain a pair of doubly linked carbon atoms.

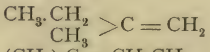
The nature of the binding of the carbon atoms in polymerization is, in all probability, influenced by the different structure of the alkylens. The manner of formation and structure of the isodibutylene produced from isobutylene correspond to the formulas:

$$\underset{\text{2 Mols. Isobutylene.}}{(CH_3)_2C:CH_2 + CH_2:C(CH_3)_2} = \underset{\text{Isodibutylene.}}{(CH_3)_3C.CH:C(CH_3)_2}.$$

Tertiary butyl alcohol very probably figures as an intermediate product, and afterward unites with a second molecule of isobutylene, and condenses to isodibutylene (compare p. 92).

Although ethylene suffers no alteration, yet its unsymmetrical halogen substitution products polymerize very readily (see p. 106).

Below are given the boiling points of some of the homologues of ethylene. It is most convenient to designate these as alkyl substitution products of ethylene.

Propylene, ...	$CH_3CH = CH_2$	— 40° gaseous.
Ethyl-ethylene, ...	$CH_3CH_2CH = CH_2$	— 5°
Sym. Dimethyl-ethylene, . . .	$CH_3.CH = CH.CH_3$	+ 1°
Unsym. Dimethyl-ethylene, . .	$(CH_3)_2C = CH_2$	— 6°
Nor. Propyl-ethylene, ... α-Amylene	$CH_3CH_2CH_2CH = CH_2$	+ 39°
Isopropyl-ethylene, ... α-Isoamylene	$(CH_3)_2CH.CH = CH_2$	+ 21°
Sym. Methyl-ethyl-ethylene, . . β-Amylene	$CH_3.CH_2.CH = CH.CH_3$	+ 36°
Unsym. Methyl-ethyl-ethylene, . γ-Amylene	 $\begin{matrix}CH_3.CH_2\\CH_3\end{matrix}{>}C = CH_2$	+ 31°
Trimethyl-ethylene, ... β-Isoamylene	$(CH_3)_2C = CH.CH_3$	+ 36°
Tetramethyl-ethylene, ...	$(CH_3)_2C = C(CH_3)_2$	+ 73° (B. 27, 454).

Many other higher members of this series are known. Of these, trimethyl-ethylene or β-isoamylene, *pental*, possesses a significance, as it is used to produce temporary narcosis, and in the preparation of the so-called *amylene hydrate* or tertiary amyl alcohol. β-Isoamylene constitutes the chief ingredient of the mixture of olefines resulting from the action of zinc chloride upon the amyl alcohol of fermentation (A. 190, 332).

HYDROCARBONS, C_nH_{2n-2}.

Two groups of hydrocarbons having this empiric formula exist:

The *acetylenes* or alkines with triple linking, and

The *allylenes* with two double linkages.

The allylenes are also called *diolefines*. The difference in structure is clearly shown in their different chemical deportment. It is the acetylenes (with group ≡ CH) alone which have the power of entering into combinations in which the hydrogen of the group ≡ CH is replaced by metals. The names adopted for the acetylenes by the Geneva Congress are formed by substituting the ending "ine" for the ending *yl* of alcohol radicals with like carbon content, hence the designation *alkines*.

2. ACETYLENES or ALKINES, C_nH_{2n-2}.

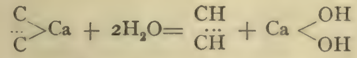
The position of acetylene, the first member of this series, among the aliphatic hydrocarbons is very important. It is the only hydrocarbon which has been prepared directly from its elements—hydrogen and carbon. Some acetylenes are distinguished by their *power of polymerization*, when they become simple *aromatic hydrocarbons*.

Acetylene [*Ethine*] $CH \equiv CH$.—Acetylene was first observed by Edmund Davy. Berthelot introduced the name acetylene and studied the hydrocarbon carefully.

(1) Berthelot effected the synthesis of acetylene by passing the electric spark between carbon points in an atmosphere of hydrogen (p. 76):

$$2C + H_2 = CH \equiv CH.$$

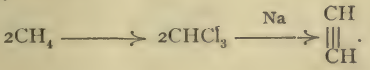
(2) It results, too, in the decomposition of the carbides of the alkaline earths by water (B. **25**, R. 850; **27**, R. 297):



$$\begin{array}{c}C\\ \vdots\\ C\end{array}\!\!>Ca + 2H_2O = \begin{array}{c}CH\\ \vdots\\ CH\end{array} + Ca\!<\!\begin{array}{l}OH\\ OH\end{array}$$

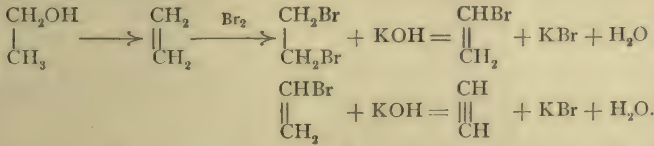
Since calcium carbide can now be obtained without trouble, the method has been used to make acetylene in quantity. The product is, however, always contaminated by phosphine, which can be removed by washing it with bromine water. The great expectations entertained, that acetylene from calcium carbide would prove a rival of gas from coal, have not yet been realized.

(3) It may be prepared from methane through the instrumentality of chloroform, from which chlorine is removed on heating it with copper or metallic sodium (Fittig). Bromoform, $CHBr_3$ (B. **25**, R. 108), and iodoform, CHI_3, are very readily changed by silver or zinc dust into acetylene:



$$2CH_4 \longrightarrow 2CHCl_3 \xrightarrow{Na} \begin{array}{c}CH\\ |||\\ CH\end{array}.$$

(4) Formerly acetylene was always made from ethylene bromide by the action of alcoholic caustic potash (A. **191**, 268). At first the ethylene bromide loses a molecule of hydrogen bromide and becomes monobrom-ethylene or vinyl bromide, which in turn loses a molecule of hydrogen bromide with the production of acetylene:

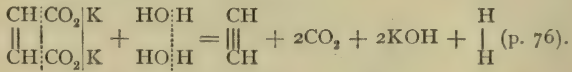


$$\begin{array}{l}CH_2OH\\ |\\ CH_3\end{array} \longrightarrow \begin{array}{l}CH_2\\ \|\\ CH_2\end{array} \xrightarrow{Br_2} \begin{array}{l}CH_2Br\\ |\\ CH_2Br\end{array} + KOH = \begin{array}{l}CHBr\\ \|\\ CH_2\end{array} + KBr + H_2O$$

$$\begin{array}{l}CHBr\\ \|\\ CH_2\end{array} + KOH = \begin{array}{l}CH\\ |||\\ CH\end{array} + KBr + H_2O.$$

As ethylene is invariably obtained from ethyl-alcohol and sulphuric acid, this method allies acetylene genetically with ethyl alcohol.

(5) Acetylene is further produced by the electrolysis of the alkali salts of the two isomeric dicarboxylic acids—maleïc and fumaric (Kekulé, A. **131**, 85):



$$\begin{array}{l}\mathrm{CH}\vdots\mathrm{CO_2}|\mathrm{K}\\ \|\quad\vdots\\ \mathrm{CH}\vdots\mathrm{CO_2}|\mathrm{K}\end{array} + \begin{array}{l}\mathrm{HO}\vdots\mathrm{H}\\ \quad\ \ \vdots\\ \mathrm{HO}\vdots\mathrm{H}\end{array} = \begin{array}{l}\mathrm{CH}\\ |||\\ \mathrm{CH}\end{array} + 2CO_2 + 2KOH + \begin{array}{l}\mathrm{H}\\ |\\ \mathrm{H}\end{array} \text{(p. 76).}$$

(6) It is worthy of note that potassium acetylene-monocarboxylate and silver acetylene-dicarboxylate are readily converted, when warmed with water, into carbon dioxide and acetylene, also silver acetylide (A. **272**, 139). The stability of the dicarboxylic acids is very much influenced by the manner of union of the carbon atoms, to which the carboxyl groups are attached.

$$C_4O_4Ag_2 = C_2Ag_2 + 2CO_2.$$

Acetylene is further formed when many carbon compounds, like alcohol, ether, marsh gas, methylene, etc., are exposed to intense heat (their vapors conducted through tubes heated to redness). Hence it is present in small amount in illuminating gas, to which it imparts a peculiar odor.

Properties.—Pure acetylene is a gas of ethereal, agreeable odor, and may be liquefied at +1° and under a pressure of 48 atmospheres. It solidifies when rapidly vaporized and then melts at —81°. It is slightly soluble in water; more readily in alcohol and ether. It burns with a very smoky flame and with air (9 vols.), but especially with oxygen (2½ vols.), forms an exceedingly explosive mixture.

Changes.—Nascent hydrogen converts acetylene into C_2H_4 and C_2H_6. Ordinary hydrogen (2 vols.) and acetylene (1 vol.) passed over platinum black form C_2H_6. (B. **7**, 352). Acetylene combines with ClH and HI, forming CH_3CHCl_2 and CH_3CHI_2.

Acetylene reacts very energetically with chlorine gas. It forms a crystalline compound with $SbCl_5$, but heat changes this to dichlor-ethylene, CHCl : CHCl and $SbCl_3$. With bromine it forms $C_2H_2Br_2$ and $C_2H_2Br_4$ (A. **221**, 138).

In contact with $HgBr_2$ and other mercury salts acetylene unites with water to yield *aldehyde*, which is also produced when acetylene is heated with water to 325° (B. **28**, R. **174**).

In contact with caustic potash and air it changes in diffused sunlight to *acetic acid*.

Acetylene polymerizes at a red heat. Three molecules unite to one molecule of *benzene*, C_6H_6. This is one of the most striking transitions from the aliphatic to the aromatic series and is, at the same time, a synthesis of the parent hydrocarbon of aromatic substances (Berthelot).

This conversion will take place at the ordinary temperature if acetylene be passed over pyrophoric iron, nickel, cobalt, or platinum sponge (B. **29**, R. 540).

Metallic Derivatives of Acetylene.—The two hydrogen atoms of acetylene can be replaced by metals. The alkali and alkaline earth acetylides are stable even in the heat, but are decomposed by water with the liberation of acetylene. Copper and silver acetylides when dry are exceedingly explosive. They are stable in the presence of water. Acids evolve pure acetylene from them.

Sodium acetylides, $CH \equiv CNa$ and $CNa \equiv CNa$.—These are produced when sodium is heated in acetylene gas. *Calcium acetylide* or *calcium carbide*, C_2Ca, is formed when calcium oxide is reduced by carbon at a red heat (Wöhler, 1862), and when a mixture of *calcium oxide* and *sugar carbon* is heated in electric furnaces to 3500° (Moissan, B. **27**, R. 238). It is a homogeneous, black fusion with a crystalline fracture. Drop fragments of calcium carbide into a tall glass cylinder filled with saturated chlorine water, when the liberated acetylene will combine with the chlorine with the production of flame. Gas-bubbles, giving out light, rise in the liquid and when they reach the surface burn there with a smoky flame. **Lithium carbide,** C_2Li_2 (B. **29**, R. 210).

Silver acetylide, C_2Ag_2, a white precipitate, and **copper acetylide,** C_2Cu_2 (B. **25**, 1097; **26**, R. 608; **27**, R. 466), a red precipitate, are formed on conducting acetylene into ammoniacal silver or cuprous solutions. The dry salts explode violently when they are heated. The silver salt even does this when gently rubbed with a glass rod. In a solution of silver nitrate acetylene precipitates the compound $HC \equiv CAg.NO_3Ag$ (B. **28**, 2108). Pure acetylene is set free by acids from these metallic compounds. The copper salt serves for the detection of acetylene in a mixture of gases. **Mercury acetylide,** C_2Hg, is thrown out as a white precipitate from alkaline solutions of mercuric oxide. It explodes violently when heated rapidly. **Acetylene mercuric chloride,** $C_2(HgCl)_2$, is precipitated on passing acetylene through solutions of corrosive sublimate. It is not explosive (B. **27**, R. 83, 466).

Acetylene Homologues.—The diolefines are isomeric with the homologues of acetylene. They contain a like number of carbon atoms, *e.g.*, allene, — $CH_2 = C = CH_2$, is isomeric with methyl acetylene, — $CH_3 . C \equiv CH$, allylene, and divinyl, $CH_2 : CH . CH : CH_2$, with dimethyl acetylene, $CH_3 . C \vdots C . CH_3$, crotonylene.

Its higher homologues, just like acetylene, are mostly prepared from the mono-halogen and dihalogen substitution products of the olefines, the *olefine dibromides*, by the action of alcoholic potash, *e. g.*, from $CH_3CCl{=}CH_2$: *allylene;* from $CH_3 . CHBr . CHBr . CH_3$: *crotonylene*, $CH_3C \equiv C . CH_3$. In this manner a host of higher acetylene homologues have been prepared from the dibromides of the higher olefines (B. **25**, 2243).

When heated to a high temperature with alcoholic potash the acetylene formed frequently sustains a *transposition;* thus, ethyl acetylene, $C_2H_5.C \equiv CH$, yields dimethyl acetylene, $CH_3.C \equiv C.CH_3$, and propyl acetylene, $C_3H_7.C \equiv CH$, furnishes ethyl methyl acetylene, $C_2H_5 . C \equiv C . CH_3$, etc. (B. **20**, R. 781). Symmetrically constituted bodies are formed from unsymmetrical compounds.

The reverse transposition sometimes occurs on heating with metallic sodium: ethyl methyl acetylene passes into propyl acetylene, and dimethyl allene, $(CH_3)_2C = C = CH_2$, yields isopropyl acetylene, etc. (B. **21**, R. 177).

Acetylenes also arise in the electrolysis of unsaturated dibasic acids. Thus *allylene* is formed in the electrolysis of the alkali salts of mesaconic and citraconic acids.

Acetylene and its homologues unite with hydrogen to form olefines, which in turn pass into paraffins. By adding the haloid acids or the halogens the mono- and di-haloid olefines are formed. The further addition of haloid acids and halogens to these yields di-, tri-, and tetra-halogen substitution products of the paraffins.

Hypochlorous acid converts the alkines into dichlor-acetones, *e. g.*, α-dichlor-propyl methyl ketone—$CH_3CH_2CCl_2.CO.CH_3$ (B. **28**, R. 781)—and water are obtained from methyl ethyl acetylene and the acid: $C_2H_5C \equiv C . CH_3 + 2ClOH$. Ketones are formed when the alkyl acetylenes are heated with water to 325° (B. **27**, R. 750; **28**, R. 173).

A characteristic of all mono-alkyl-acetylenes, as well as of acetylene itself, is their power to yield solid crystalline compounds by the action of ammoniacal solutions of silver and cuprous salts. Hydrochloric acid will again liberate the acetylenes from these salts. The behavior affords a very convenient method for separating the acetylenes from other gases, as well as for obtaining them in a pure condition.

The acetylenes are absorbed by concentrated sulphuric acid; some even polymerize to aromatic derivatives.

In the presence of $HgBr_2$ and other salts of mercury, the acetylenes can unite with water. In this way we get from acetylene, aldehyde, C_2H_4O, from allylene, C_3H_4, acetone, C_3H_6O, from valerylene, C_5H_8, a ketone, $C_5H_{10}O$ (B. 14, 1540, and 17, 28). Very often moderately dilute sulphuric acid will act in the same way (see Allylene).

The boiling points of some of the acetylenes are as follows:

		B. P.
Allylene, Methyl-acetylene [Propine]	$CH_3C \equiv CH$	Gas
Crotonylene, Dimethyl Acetylene [2-Butine]	$CH_3C \equiv CCH_3$	27–28°
Ethyl Acetylene [3-Butine]	$C_2H_5C \equiv CH$	18°
Methyl Ethyl Acetylene [3-Pentine]	$C_2H_5C \equiv CCH_3$	55–56°
Norm. Propyl Acetylene [4-Pentine]	$n\text{-}C_3H_7C \equiv CH$	48–49°
Isopropyl Acetylene [3-Methyl-1-Butine]	$(CH_3)_2CH . C \equiv CH$	28–29°

Allylene and *crotonylene* deserve consideration, because when brought in contact with concentrated sulphuric acid they pass into symmetric *trimethyl benzene* and *hexamethyl benzene*.

$$3CH_3C \equiv CH \longrightarrow C_6H_3[1,3,5](CH_3)_3\text{—Mesitylene.}$$
$$3CH_3C \equiv CCH_3 \longrightarrow C_6(CH_3)_6\text{—Hexamethyl Benzene.}$$

3. DIOLEFINES, C_nH_{2n-2}.

The diolefines are not capable of forming silver and copper compounds. They do give precipitates with mercuric sulphate and chloride in aqueous solution (B. **21**, R. 185, 717; **24**, 1692).

The "Geneva names" for the diolefines are derived by inserting a "di," for the number of double linkages, before the final syllable "ene"—*e. g.*, [propadiëne] for symmetric allylene.

The hydrocarbons of this class are numerous. Some of them are worthy of note because of their genetic relations. They are:

1. Allene, sym. allylene [Propadiēne]	$CH_2=C=CH_2$	Gas
2. Divinyl, Erythrene [1, 3-Butadiēne] Pyrrolylene	$CH_2=CH—CH=CH_2$	Gas
3. Piperylene [1, 4-Pentadiēne]	$CH_2=CH—CH_2—CH=CH_2$	42°
4. Isoprene	$CH_2=CH—C(CH_3)=CH_2$ (?)	35°
5. Diallyl [1, 5-Hexadiēne]	$CH_2=CH—CH_2—CH_2—CH=CH_2$	59.3°
6. Conylene [1, 4-Octadiēne]	$CH_2=CH—CH_2—CH=CH.CH_2.CH_2.CH_3$	126°.

Symmetric allylene has been obtained by the electrolysis of potassium itaconate (p. 76).

Divinyl, Erythrene, or **Pyrrolylene** is found in compressed illuminating gas. and serves as the starting-out material for the synthesis of erythrol, which yields it on boiling with formic acid. It is called pyrrolylene because it is formed in the breaking down of pyrrolidine or tetra-hydropyrrol (see this) (B. **19**, 569).

Piperylene and **Conylene** are formed in the same manner from piperidine (see this) and coniïne (see this) (B. **14**, 665, 710).

Isoprene, a distillation product of caoutchouc, is closely related to the terpenes. It is called a *hemiterpene*, and by spontaneous polymerization passes into dipentene or cinene, and then back into caoutchouc (B. **25**, R. 644).

Diallyl is formed from allyl iodide by means of sodium (see hexyl-erythrol).

4. OLEFINACETYLENES.

By this name are understood the hydrocarbons containing both doubly and trebly linked pairs of carbon atoms in their molecules. Many of them are known, but none deserve special consideration.

5. DIACETYLENES, C_nH_{2n-6}.

Diacetylene, $HC\vdots C.C\vdots CH$, is formed from diacetylene dicarbonic acid. It is a gas that yields a yellow precipitate with an ammoniacal silver solution. The two hydrocarbons, dipropargyl and dimethyl-di-acetylene, are isomeric with benzene.

Dipropargyl, $CH\vdots C.CH_2.CH_2.C\vdots CH$, is formed on warming solid crystalline diallyltetrabromide, $C_6H_{10}Br_4$, with KOH. It is a very mobile liquid, of penetrating odor, and boiling at 85°. It forms copper and silver derivatives. If dipropargyl be allowed to stand, it becomes resinous.

Dimethyl Di-acetylene, $CH_3.C\equiv C.C\equiv C.CH_3$, has been obtained from the copper derivative of allylene. It melts at 64° and boils at 130° (B. **20**, R. 564).

HALOGEN DERIVATIVES OF THE HYDROCARBONS.

The halogen substitution products result from the replacement of hydrogen in the hydrocarbons by the halogens. In the discussion of the methods of formation and the transpositions of the saturated and unsaturated aliphatic hydrocarbons, their haloid derivatives were constantly encountered. We have also learned the methods of producing these alkylogens, proceeding from the hydrocarbons. They are:

(1) *Formation by the direct substitution of the limit hydrocarbons.* It was emphasized in the case of methane (p. 82) and ethane (p. 83) that these hydrocarbons, usually so very stable, were attacked by chlorine. A molecule of hydrogen chloride is produced for every

hydrogen atom replaced by chlorine, until the entire hydrogen content is substituted. Methane, CH_4, yields tetra- or perchlormethane, CCl_4, while ethane gives hexa- or perchlorethane, C_2Cl_6.

The action of chlorine is accelerated by, and very often also dependent upon, direct sunlight or the presence of small quantities of iodine. It is the ICl_3, which arises in the latter case, that facilitates the reaction. $SbCl_5$ also plays the rôle of a chlorine carrier, since upon heating it yields $SbCl_3$ and 2Cl. In very energetic chlorination the carbon chain is ruptured (B. **8**, 1296; **10**, 801).

The final products are CCl_4 and hexa- or perchlorbenzene, C_6Cl_6, with perchlorethane, C_2Cl_6, and perchlormesole, C_4Cl_6, as intermediate products (B. **24**, 1011).

Heat hastens the action of bromine. Its action is also accelerated by sunlight or with $AlBr_3$ as a carrier.

Iron is an excellent carrier of chlorine, bromine, and iodine. Its action seems to be due to the formation and decomposition of compounds with ferric halides (A. **225**, 196; **231**, 158). When iron is used as a bromine carrier every normal hydrocarbon passes into that bromide, which contains just as many bromine atoms as it has carbon atoms (B. **26**, 2436); a bromine atom attaches itself to each carbon atom.

Usually iodine does not replace well, inasmuch as the final iodine products sustain reduction through the hydriodic acid formed simultaneously with them:

$$C_3H_7I + HI = C_3H_8 + I_2.$$

In the presence of substances (like HIO_3 and HgO) capable of uniting or decomposing HI, iodine frequently effects substitution:

$$\begin{aligned} 5C_3H_8 + 2I_2 + IO_3H &= 5C_3H_7I + 3H_2O \\ 2C_3H_8 + 2I_2 + HgO &= 2C_3H_7I + H_2O + HgI_2. \end{aligned}$$

In direct substitution a mixture of mono- and poly-substitution products generally results, and these are separated by fractional distillation or crystallization.

(2) The unsaturated aliphatic hydrocarbons, the olefines (p. 93) and acetylenes (p. 98) add hydrochloric, hydrobromic, and especially hydriodic acids. The haloid acid is dissolved in glacial acetic acid (B. **11**, 1221), or it is applied in concentrated aqueous solution.

(3) The free halogens are absorbed by the unsaturated hydrocarbons with more avidity than the haloid acids (p. 89).

Two additional reactions (already indicated in the preceding remarks as existing) proceed from oxygen-containing aliphatic derivatives to halogen substitution products:

(4) Replacement of the hydroxyl groups of the alcohols by fluorine, chlorine, bromine, or iodine by means of the haloid acids or by means of the phosphorus halides (p. 116).

(5) By the action of phosphorus pentachloride and phosphorus chlorbromide, or phosphorus pentabromide upon aldehydes and ketones.

These last methods of formation will be more thoroughly discussed under the individual groups of halogen substitution products.

Transpositions of the Halogen Derivatives.—The iodine derivatives of the halogen substitution products are the most unstable. In the light they rapidly acquire a red color, with the separation of iodine. The chlorides and bromides, rich in hydrogen, burn with a green-edged flame (p. 24).

(1) Nascent hydrogen (zinc and hydrochloric acid or glacial acetic acid, sodium amalgam and water) can reconvert all the halogen derivatives, by successive removal of the halogen atoms, into the corresponding hydrocarbons (p. 83):

$$CHCl_3 + 3H_2 = CH_4 + 3HCl.$$

This change is called a *retrogressive* substitution.

(2) Alcoholic sodium and potassium hydroxides occasion the splitting off of an halogen hydride, and the production of unsaturated compounds (p. 91):

$$\underset{\text{Propyl Bromide.}}{CH_3 . CH_2 . CH_2Br} + KOH = \underset{\text{Propylene.}}{CH_3 . CH : CH_2} + KBr + H_2O.$$

In this reaction the halogen attracts to itself the hydrogen of the least hydrogenized adjacent carbon atom (compare p. 93). Such a splitting sometimes occurs on application of heat.

A. HALOGEN PARAFFINS.

1. MONOHALOGEN PARAFFINS, ALKYLOGENS, ALKYL HALIDES, $C_nH_{2n} + {}_1X$.

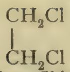
These are genetically connected by reactions to the alcohols, which are almost always employed in their preparation. It is impossible to obtain mono-iodo-paraffins by direct substitution. On comparing the formulas of the alkylogens with those of the halogen hydrides,

$$\begin{array}{ccccc} HFl & HCl & HBr & HI & H.OH \\ C_2H_5Fl & C_2H_5Cl & C_2H_5Br & C_2H_5I & C_2H_5.OH \end{array}$$

it will be seen that they can be regarded as haloid acids, in which the hydrogen atoms have been replaced by hydrocarbon residues. As the latter, together with the water residue, constitute the monohydric (monacid) alcohols, they are called alcohol radicals or alkyls. Acids, the hydrogen of which is replaceable by metals, yield acid esters when alcohol radicals are substituted for that hydrogen. The monohalogen alkyls are therefore discussed as *haloid esters*, at the head of the acid esters of the monacid alcohols.

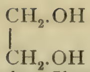
2. DIHALOGEN PARAFFINS, $C_nH_{2n}X_2$.

(*a*) Dihalogen paraffins, where two halogen atoms are attached to two different carbon atoms, may be viewed as the haloid esters of diacid paraffin alcohols or glycols. They can be derived from these and will be considered together with them:



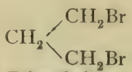
$$\begin{array}{l} CH_2Cl \\ | \\ CH_2Cl \end{array}$$

Ethylene Chloride.

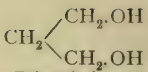


$$\begin{array}{l} CH_2.OH \\ | \\ CH_2.OH \end{array}$$

Ethylene Glycol.

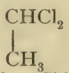


Trimethylene Bromide.



Trimethylene Glycol.

(*b*) Dihalogen paraffins, the two halogen atoms of which are attached to the same carbon atom, may be termed *aldehyde-halides*, if the carbon atom is terminal, and *ketone-halides*, when the carbon atom occupies an intermediate position. Indeed, these compounds can be obtained from the aldehydes and ketones by means of phosphorus halides. They will, therefore, be discussed after the aldehydes and the ketones:

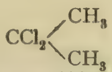


$$\begin{array}{l} CHCl_2 \\ | \\ CH_3 \end{array}$$

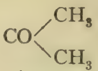
Ethylidene Chloride
Aldehyde Chloride.

$$\begin{array}{l} CHO \\ | \\ CH_3 \end{array}$$

Acetaldehyde.



Acetone Chloride
β-Dichlor-propane.



Acetone.

It must be remarked here that the unsymmetric ethane dihalides—*e.g.*, $CH_3 . CHCl_2$, ethylidene chloride—have lower boiling points and lower specific gravities than the corresponding symmetric isomerides,—*e.g.*, ethylene chloride, $CH_2Cl . CH_2Cl$.

3. PARAFFIN POLYHALIDES.

The paraffin polyhalides, containing but one halogen atom to each carbon atom, will be discussed after the corresponding polyacid paraffin alcohols.

The simplest and most important representatives of the paraffin trihalides, in which three halogen atoms are attached to the same carbon atom, are the *methane trihalides:*

$CHCl_3$	$CHBr_3$	CHI_3
Chloroform.	Bromoform.	Iodoform.

They are so intimately related to formic acid and its derivatives that they will be considered after this acid.

The most important paraffin *tetrahalides* are the *methane tetrahalides.* They bear the same relation to carbonic acid that the methane trihalides sustain to formic acid. They will, therefore, be treated after carbonic acid:

CFl_4	CCl_4	CBr_4	CI_4
Methane Tetrafluoride.	Methane Tetrachloride.	Methane Tetrabromide.	Methane Tetraiodide.

These compounds are also called methane perhalides, to indicate that all the hydrogen in them is completely replaced by halogens.

Polyhalide Ethanes.—The following table contains the boiling points of the known polychlor- and polybrom-ethanes:

Name.	Formula.	M. P.	B. P.	Formula.	M. P.	B. P.
Vinyl Trichloride *β*-Trichlor-ethane	$CHCl_2$ $\dot{C}H_2Cl$	—	114°	$CHBr_2$ $\dot{C}H_2Br$	—	187–188°
Ethenyl Trichloride *α*-Trichlor-ethane Methyl Chloroform	CCl_3 $\dot{C}H_3$	—	74.5°	—	—	—
Acetylene Tetrachloride Symmetrical	$CHCl_2$ $\dot{C}HCl_2$	—	147°	$CHBr_2$ $\dot{C}HBr_2$	—	102° (12 mm.)
Acetylidene Tetrachloride Unsymmetrical	CCl_3 $\dot{C}H_2Cl$	—	129–130°	CBr_3 CH_2Br	—	105° (13.5 mm.)
Pentachlor-ethane	CCl_3 $\dot{C}HCl_2$	—	159°	CBr_3 $\dot{C}HBr_2$	54°	decomposes
Perchlor-ethane	CCl_3 $\dot{C}Cl_3$	187°	sublimes	CBr_3 $\dot{C}Br_3$	—	decomposes at 200–210° without decomposition.

For the relations existing between the boiling points and specific volumes of the halogen substitution products of the ethanes, see B. **15**, 2559. As to the refractive power of the brominated ethanes, see Z. phys. Ch. **2**, 236.

The polychlor- and polybrom-ethanes have few genetic relationships with the oxygen compounds corresponding to them. The methods of formation and the transpositions of the polysubstituted ethanes are most intimately related to the methods of formation and the transpositions of the halogen substitution products of the ethylenes and acetylenes, a tabular view of which will be given in the following section. They will, therefore, precede the discussion of the latter.

It may be merely mentioned here that by the action of chlorine upon ethyl chloride and ethylidene chloride in sunlight *methyl-chloroform* or *a-trichlor-ethane*, CH_3CCl_3, will be produced. together with *vinyl trichloride*, $CH_2Cl . CHCl_2$. The further action of chlorine upon the trichlorethanes produces: $CH_2Cl . CCl_3$, $CHCl_2 . CCl_3$, perchlor-ethane, $CCl_3 . CCl_3$. $CHCl_2 . CHCl_2$ is formed from acetylene dichloride and chlorine, as well as from dichloraldehyde by means of phosphorus pentachloride (B. **15**, 2563). Only methyl chloroform, $CH_3 . CCl_3$, related to acetic acid the same as chloroform is to formic acid, will be further described, together with the chlorides of the fatty acids.

Perchlor-ethane, C_2Cl_6, is a crystalline mass, with a camphor-like odor. Its specific gravity equals 2.01. It melts at 187–188° (corr.). It sublimes at the ordinary pressure, as its critical pressure lies below 760 mm. It boils at 185.5° under a pressure of 776.7 mm. When its vapors are conducted through a tube heated to redness it breaks down into Cl_2 and *perchlorethylene.* It yields the latter compound when it is treated with potassium sulphide.

a-Tribromethane, $CH_3 . CBr_3$, has not yet been prepared.

Acetylene Tetrabromide, $CHBr_2 . CHBr_2$, is obtained from acetylene and bromine. Zinc dust and alcohol convert it into acetylene dibromide (A. **221**, 141), while benzene and $AlCl_3$ change it into *anthracene* (see this.)

Perbromethane, C_2Br_6, is a colorless, crystalline compound, dissolving with difficulty in alcohol and ether. It breaks down at 200° into bromine and *perbromethylene*, C_2Br_4.

Five structural cases are possible for trisubstituted propane. The most important of these derivatives have the structure $CH_2X.CHX.CH_2X$, corresponding to glycerol, $CH_2(OH) . CH(OH) . CH_2(OH)$. They will be discussed after the latter.

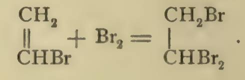
Mixed Halogen Substitution Products of the Paraffins.—There are numerous paraffins containing different halogens side by side in the same molecule.

B. HALOGEN DERIVATIVES OF THE OLEFINES.

As a general thing, the halogen substitution products of the unsaturated hydrocarbons cannot be prepared by direct action of the halogens, since addition products are apt to result (p. 89). They are produced, however, by the moderated action of alcoholic potash, or Ag_2O, upon the disubstituted hydrocarbons $C_nH_{2n}X_2$. This reaction occurs very readily if we employ the addition products of the olefines:

$$\underset{\substack{\text{Ethylene}\\\text{Chloride.}}}{C_2H_4Cl_2} + KOH = \underset{\substack{\text{Monochlor-}\\\text{ethylene.}}}{C_2H_3Cl} + KCl + H_2O.$$

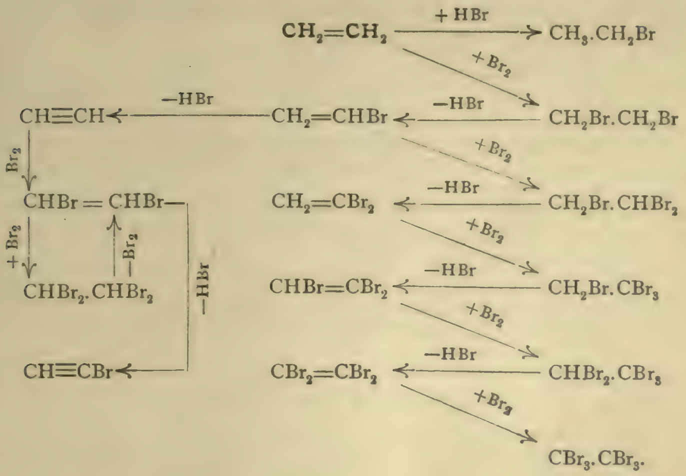
When the alcoholic potash acts very energetically, the hydrocarbons of the acetylene series are formed (p. 95). Being unsaturated compounds they unite directly with the halogens, and also the hydrides of the latter:



$$\begin{matrix} CH_2 \\ \| \\ CHBr \end{matrix} + Br_2 = \begin{matrix} CH_2Br \\ | \\ CHBr_2 \end{matrix} .$$

These reactions indicate that ethylene is the starting-out substance for the preparation of nearly all the halogen substitution products of the ethanes and ethylenes, as well as for the preparation of acetylene.

The following diagram represents how, by the addition of bromine and the splitting-off of hydrogen bromide, the bromine substitution derivatives of the ethanes are connected with ethylene, with the ethylene bromine derivatives, and with acetylene (A. **221**, 156):



Vinyl Chloride, $CH_2=CHCl$, and **Vinyl Bromide**, $CH_2=CHBr$, are obtained from ethylene chloride and ethylene bromide by the action of alcoholic potash, which, by continued action upon them, produces acetylene. The group $CH_2=CH—$ is called *vinyl.*

The boiling points of the *chlorinated* and *brominated ethylenes* are given in the following table:

	Formula.	B. P.	Formula.	B. P.
Vinyl Chloride, Monochlorethylene, ...	$CH_2=CHCl$	−18°	$CH_2=CHBr$	+16°
Acetylene Dichloride, sym. Dichlorethylene, ...	$CHCl=CHCl$	+55°	$CHBr=CHBr$	110°
Acetylidene Dichloride, unsym. Dichlorethylene,	$CH_2=CCl_2$	+37°	$CH_2=CBr_2$	91°
Trichlor-ethylene, ...	$CHCl=CCl_2$	88°	$CHBr=CBr_2$	164°
Tetrachlor ethylene, Perchlor-ethylene, ...	$CCl_2=CCl_2$	121°	$CBr_2=CBr_2$	M. P. 53°
Tetra-iodo-ethylene (B. **26**, R. 289; **29**, 1411),	. . .	. . .	$CI_2=CI_2$	187°

Consult A. **221**, 156, for the boiling point relations of the brom-ethanes and brom-ethylenes. The unsymmetrical compounds, $CH_2=CHCl$, $CH_2=CHBr$, $CH_2=CCl_2$ and $CH_2=CBr_2$, polymerize quite easily (B. **12**, 2076). $CH_2=CBr_2$ and $CHBr=CBr_2$ yield $CH_2Br.COBr$, brom-acetyl bromide, and $CHBr_2COBr$, dibrom-acetyl bromide (B. **16**, 2919; **21**, 3356) with oxygen. Ozonized air converts perchlorethylene into phosgene, $COCl_2$, and trichloracetyl chloride (B. **27**, R. 509). Consult A. **235**, 150, 299, for the action of $AlCl_3$ on polybrom-ethanes and ethylenes, in the presence of benzene.

See B. **26**, R. 18, 19, for the addition of iodine to acetylenes.

Three different mono-halogen products are derived from propylene, $CH_3 — CH = CH_2$:

(1) $CH_3 — CH = CHX$	(2) $CH_3 — CX = CH_2$	(3) $CH_2X — CH = CH_2$.
α-Derivatives.	β-Derivatives.	γ-Derivatives.

(1) The α-derivatives are obtained from the propylidene compounds, $CH_3.CH_2.CHX_2$ (from propyl aldehyde), when the latter are heated with alcoholic potassium hydroxide.

(2) The β-derivatives, $CH_3.CX:CH_2$, are prepared in pure condition from the halogen compounds, $CH_3.CX_2.CH_3$ (p. 102), derived from acetone.

(3) The γ-derivatives of propylene, $CH_2X — CH = CH_2$, are designated *Allyl haloids*, because they correspond to allyl alcohol, $CH_2:CH.CH_2OH$. They will be described after the alkylogens.

C. HALOGEN ACETYLENES.

Acetylene Chloride, C_2HCl, has been obtained from dichlor-acrylic acid, $CCl_2 = CH.CO_2H$, by the action of baryta. It is an explosive gas (A. **203**, 88; B. **23**, 3783).

Acetylene Bromide, C_2HBr, obtained from the dibromide by means of alcoholic potash, is a gas, inflaming in air contact.

Acetylene Iodide, C_2HI, is formed on boiling potassium iodopropargylate with water (B. **18**, 2274).

Acetylene Di-iodide, C_2I_2, is produced when iodine acts upon silver acetylide. It melts with decomposition at 78°. It changes largely to ethylene tetraiodide (B. **29**, 1411) in the light or when it is heated.

The halogen acetylene derivatives polymerize more easily than acetylene itself. The products are in part benzene derivatives: monobrom-acetylene yields tribrom-benzene.

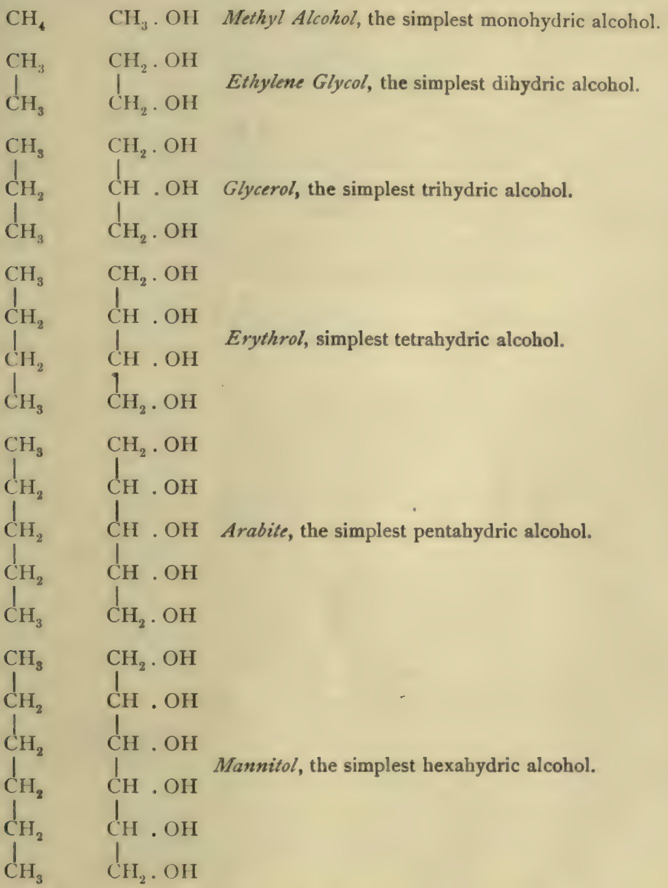
$3CH \equiv CBr = C_6H_3Br_3$;	$3CH \equiv CI = C_6H_3I_3$;	$3CI \equiv CI = C_6I_6$.
Tribrom-benzene.	Tri-iodo-benzene.	Hexa-iodo-benzene.

Perchlormesole, $C_4Cl_6 = CCl_3.C \equiv C.CCl_3$ (?) or $CCl_2 = CCl — CCl = CCl_2$ (?), may be mentioned here. It frequently appears in exhaustive chlorinations. It melts at 39° and boils at 284° (B. **10**, 804; compare B. **22**, 1269).

OXYGEN DERIVATIVES OF THE METHANE HYDROCARBONS.

We became acquainted with the simplest linkings of the carbon atoms in studying the aliphatic hydrocarbons and their halogen substitution products. The derivatives next in order are the oxygen compounds. They furnish further cause for the classification of the carbon compounds. We may consider them as formed from the aliphatic hydrocarbons by the substitution of the univalent water residue—the hydroxyl group—OH, for hydrogen.

But one or several hydroxyl groups attach themselves to each carbon atom. In the first instance alcohols result. These are neutral compounds, closely related in many respects to water. Alcohols, according to the number of hydroxyl groups present in them, are classified as mono-, di-, tri-, and poly-hydric, because in the alcohols with one hydroxyl a univalent radical, and in those with two hydroxyls a bivalent radical, etc., is in union with the water residues. Therefore, the simplest monohydric alcohol contains one carbon atom, the simplest dihydric alcohol two carbon atoms, etc., as indicated in the following arrangement:



$CH_4 \qquad CH_3 . OH$ *Methyl Alcohol*, the simplest monohydric alcohol.

$$\begin{array}{l} CH_3 \\ | \\ CH_3 \end{array} \qquad \begin{array}{l} CH_2 . OH \\ | \\ CH_2 . OH \end{array}$$

Ethylene Glycol, the simplest dihydric alcohol.

$$\begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ CH_3 \end{array} \qquad \begin{array}{l} CH_2 . OH \\ | \\ CH \ . OH \\ | \\ CH_2 . OH \end{array}$$

Glycerol, the simplest trihydric alcohol.

$$\begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CH_3 \end{array} \qquad \begin{array}{l} CH_2 . OH \\ | \\ CH \ . OH \\ | \\ CH \ . OH \\ | \\ CH_2 . OH \end{array}$$

Erythrol, simplest tetrahydric alcohol.

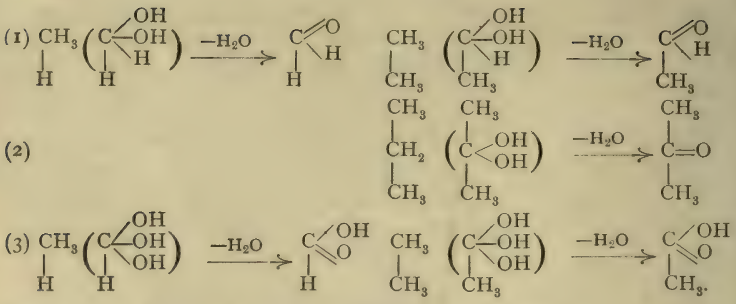
$$\begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CH_3 \end{array} \qquad \begin{array}{l} CH_2 . OH \\ | \\ CH \ . OH \\ | \\ CH \ . OH \\ | \\ CH \ . OH \\ | \\ CH_2 . OH \end{array}$$

Arabite, the simplest pentahydric alcohol.

$$\begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CH_3 \end{array} \qquad \begin{array}{l} CH_2 . OH \\ | \\ CH \ . OH \\ | \\ CH \ . OH \\ | \\ CH \ . OH \\ | \\ CH \ . OH \\ | \\ CH_2 . OH \end{array}$$

Mannitol, the simplest hexahydric alcohol.

Or, hydrogen atoms attached to the same carbon atom of hydrocarbons are replaced by —OH groups. In such cases experience teaches that, with rare exceptions, water splits off, and oxygen unites itself with its full valence to carbon. The following possibilities then arise: Two hydroxyl groups replace two hydrogen atoms of a terminal CH_3-group, or of an intermediate CH_2-group; three hydroxyl groups replace three hydrogen atoms of a terminal CH_3-group; water then always separates, *e. g.:*



Three new classes of oxygen derivatives are formed :

(1) Compounds containing the group $-\mathrm{C}\Big\langle\begin{matrix}\mathrm{O}\\ \mathrm{H}\end{matrix}$: *Aldehydes.* The group $-\mathrm{C}\Big\langle\begin{matrix}\mathrm{O}\\ \mathrm{H}\end{matrix}$ is called the aldehyde group.

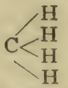
(2) Compounds containing the group $=\mathrm{C}=\mathrm{O}$ in union with two carbon atoms: *Ketones.* The group $=\mathrm{CO}$ is known as the keto- or ketone group.

(3) Compounds containing the group $-\mathrm{C}\Big\langle\begin{matrix}\mathrm{OH}\\ \mathrm{O}\end{matrix}$: *Carboxylic acids.* The group $-\begin{matrix}\mathrm{C=O}\\ \diagdown\mathrm{OH}\end{matrix}$ is called *carboxyl.* The alcohols, aldehydes, and ketones are neutral substances. The carboxylic acids are pronounced acids. They form salts in the same manner as the mineral acids.

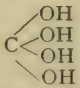
Aldehydes, ketones, and carboxylic acids are most intimately related to the mon acid alcohols. They are the oxidation products of alcohols, and will be discussed after them. Unsaturated hydrocarbons, in like manner, yield unsaturated alcohols, aldehydes, ketones, and carboxylic acids. As a rule, the unsaturated derivatives will receive attention after the saturated compounds corresponding to them ; *i. e.*, the unsaturated alcohols will follow the saturated alcohols.

Similarly, an almost endless series of oxidation products attaches itself to the di-, tri-, and poly-hydric alcohols. These have the same oxygen-containing atomic groups, as the monohydric alcohols and their oxidation products, and at the same time several in the same molecule. The multiplicity grows rapidly. It will be seen later that nine classes of oxidation products may be derived from the dihydric alcohols or glycols.

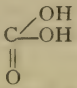
The foregoing development of the connection of aldehydes, ketones, and carboxylic acids must be completed with methane. Let us suppose in this case that the *four* hydrogen atoms are replaced by hydroxyl groups. The exit of two molecules of water would then be possible, and carbon dioxide, the anhydride of two acids not capable of existence (orthocarbonic acid and ordinary metacarbonic acid) would be obtained. The carbonates are derived from the meta acid.



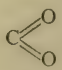
Methane.



Orthocarbonic Acid.



Metacarbonic Acid.



Carbon Dioxide.

The carbonates are salts of a dibasic acid. Therefore, carbonic acid, with its numerous derivatives, will be discussed before the dicarboxylic acids, the final oxidation products of the diacid alcohols or glycols, whose simplest representative is oxalic acid.

III. THE MONOHYDRIC ALCOHOLS AND THEIR OXIDATION PRODUCTS.

1. MONOHYDRIC ALCOHOLS.

The monohydric alcohols contain one hydroxyl group, OH; bivalent oxygen links the univalent alcohol radical to hydrogen: $CH_3 . O . H$, methyl alcohol. This hydrogen atom is characterized by its ability, in the action of acids upon alcohol, to exchange itself for acid residues, forming compound ethers or *esters*, corresponding to the salts of mineral acids:

$$\underset{\text{Ethyl Alcohol.}}{C_2H_5 . OH} + NO_2 . OH = \underset{\substack{\text{Ethyl Nitrate or}\\ \text{Nitric Ethyl Ester.}}}{C_2H_5 . O . NO_2} + H_2O.$$

Alkyls and metals can also replace the hydrogen in alcohol:

$$\underset{\text{Ethyl-methyl Ether.}}{C_2H_5 . O . CH_3} \qquad \underset{\text{Sodium Ethylate.}}{C_2H_5 . ONa.}$$

Structure of the Monohydric Alcohols.—The possible isomeric alcohols may be readily derived from the hydrocarbons. There is one possible structure for the first two members of the normal alcohols:

$$\underset{\text{Methyl Alcohol.}}{CH_3 . OH} \qquad \underset{\text{Ethyl Alcohol.}}{C_2H_5 . OH.}$$

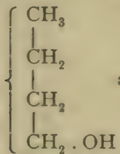
Two isomerides can be obtained from propane, $C_3H_8 = CH_3 . CH_2 . CH_3$:

$$\underset{\text{Propyl Alcohol.}}{CH_3 . CH_2 . CH_2 . OH} \quad \text{and} \quad \underset{\text{Isopropyl Alcohol.}}{CH_3 . CH(OH) . CH_3.}$$

Two isomerides correspond to the formula C_4H_{10} (p. 43):

$$\underset{\text{Normal Butane.}}{CH_3 . CH_2 . CH_2 . CH_3} \quad \text{and} \quad \underset{\text{Isobutane.}}{CH(CH_3)_3.}$$

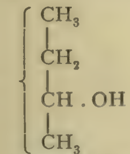
Two isomeric alcohols may be obtained from each of these:



$$\left\{\begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CH_2 . OH \end{array}\right.$$

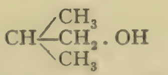
Primary Butyl Alcohol.

and



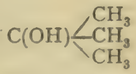
$$\left\{\begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ CH . OH \\ | \\ CH_3 \end{array}\right.$$

Secondary Butyl Alcohol.



Prim. Isobutyl Alcohol.

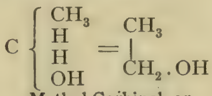
and



Tert. Isobutyl Alcohol.

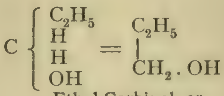
An excellent method of formulating the alcohols was introduced by

Kolbe in 1860 (A. **113**, 307; **132**, 102). He regarded all alcohols as derivatives of methyl alcohol, for which he proposed the name *carbinol*, and compared the alcohols, formed by the replacement of hydrogen, not in union with oxygen, by alcohol radicals with the primary, secondary, and tertiary amines, resulting from the replacement of the hydrogen in ammonia by alcohol radicals. With this view as a basis, Kolbe predicted the existence of secondary and tertiary alcohols. Their first representative was discovered shortly afterward. By the replacement of one hydrogen atom in carbinol by alkyls (p. 57) the *primary alcohols* result:



$$C\left\{\begin{array}{l}CH_3\\H\\H\\OH\end{array}\right. = \begin{array}{l}CH_3\\|\\CH_2 . OH\end{array}$$

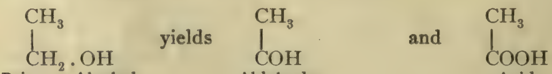
Methyl Carbinol, or
Ethyl Alcohol.



$$C\left\{\begin{array}{l}C_2H_5\\H\\H\\OH\end{array}\right. = \begin{array}{l}C_2H_5\\|\\CH_2 . OH\end{array}$$

Ethyl Carbinol, or
Propyl Alcohol.

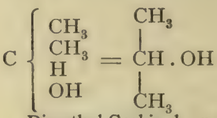
If the replacing group possesses normal structure, the primary alcohols are said to be *normal*. In alcohols of this class the carbon atom carrying the hydroxyl group has two additional hydrogen atoms (they contain the group $—CH_2 . OH$). Hence compounds of this variety may very easily pass into aldehydes (with group COH) and acids (with COOH group) on oxidation (see p. 108):



$$\begin{array}{l}CH_3\\|\\CH_2 . OH\end{array} \quad \text{yields} \quad \begin{array}{l}CH_3\\|\\COH\end{array} \quad \text{and} \quad \begin{array}{l}CH_3\\|\\COOH\end{array}$$

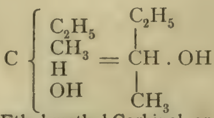
Primary Alcohol. Aldehyde. Acid.

The *secondary alcohols* result when two hydrogen atoms in carbinol, $CH_3 . OH$, are replaced by alkyls:



$$C\left\{\begin{array}{l}CH_3\\CH_3\\H\\OH\end{array}\right. = \begin{array}{l}CH_3\\|\\CH . OH\\|\\CH_3\end{array}$$

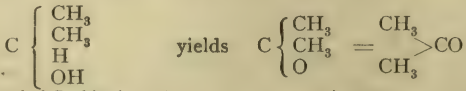
Dimethyl Carbinol, or
Isopropyl Alcohol.



$$C\left\{\begin{array}{l}C_2H_5\\CH_3\\H\\OH\end{array}\right. = \begin{array}{l}C_2H_5\\|\\CH . OH\\|\\CH_3\end{array}$$

Ethyl-methyl Carbinol, or
Isobutyl Alcohol.

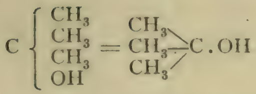
In alcohols of this class the carbon atom carrying the OH group has but one additional hydrogen atom. (They contain the group $> CH . OH$.) They do not furnish corresponding aldehydes and acids. When oxidized they pass into ketones (p. 108):



$$C\left\{\begin{array}{l}CH_3\\CH_3\\H\\OH\end{array}\right. \quad \text{yields} \quad C\left\{\begin{array}{l}CH_3\\CH_3\\O\end{array}\right. = \begin{array}{l}CH_3\\ \\CH_3\end{array}\!\!>CO$$

Dimethyl Carbinol. Acetone.

When, finally, all three hydrogen atoms in carbinol are replaced by alkyls, we get the *tertiary alcohols*, containing the group $-\!\!>C . OH$.



Trimethyl Carbinol.

The tertiary alcohols decompose when oxidized.

The secondary and tertiary alcohols, in distinction from the primary or true alcohols, are designated **pseudo-alcohols.**

The "Geneva names" for the alcohols are derived from the names of the corresponding hydrocarbons, with the addition of the final syllable "ol":

$CH_3.OH$ = [Methanol]; $CH_3.CH_2.OH$ = [Ethanol];
$CH_3.CH_2.CH_2.OH$ = [1-Propanol]; $CH_3.CHOH.CH_3$ = [2-Propanol].

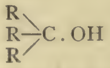
The parallels in the formulas of the three classes of alcohols and the three classes of amines (see these) are very evident upon studying the following general formulas:

$R.CH_2.OH$

Primary Alcohols.

$\begin{matrix}R\\R\end{matrix}\!>CH.OH$

Secondary Alcohols.



Tertiary Alcohols.

$R.NH_2$

Primary Amine.

$\begin{matrix}R\\R\end{matrix}\!>NH$

Secondary Amine.

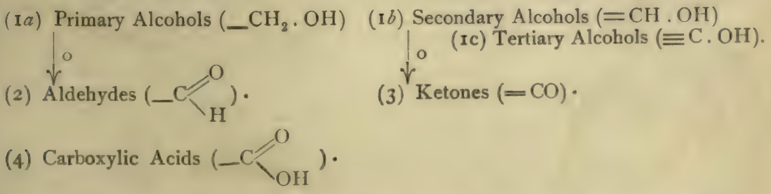
Tertiary Amine.

The deportment of alcohols on oxidation is of great importance in answering the question as to whether a certain alcohol is primary, secondary, or tertiary in its character. What has already been submitted may be summarized thus:

A *primary* alcohol on oxidation yields an *aldehyde*, which passes into an *acid* if the action be continued. This acid contains as many carbon atoms in its molecule as the parent alcohol. Oxidation changes a secondary alcohol into a *ketone*, having an equal number of carbon atoms in its molecule. A *tertiary* alcohol breaks down on oxidation into compounds having a lower carbon content.

The basis of the classification of the next section is:

The monohydric alcohols and their oxidation products:



(1*a*) Primary Alcohols ($—CH_2.OH$) (1*b*) Secondary Alcohols ($=CH.OH$)
(1c) Tertiary Alcohols ($\equiv C.OH$).

(2) Aldehydes ($—C{\begin{smallmatrix}O\\H\end{smallmatrix}}$). (3) Ketones ($=CO$).

(4) Carboxylic Acids ($—C{\begin{smallmatrix}O\\OH\end{smallmatrix}}$).

Four classes of oxygen derivatives must, therefore, be distinguished. The unsaturated derivatives attach themselves to the saturated of each class.

Formation of Alcohols.—*Review of Reactions.*—They are obtained from bodies containing a like number of carbon atoms:

(1) By the saponification of acid esters.

(2) By the reduction of polyhydric alcohols.

(3) By the action of nitrous acid upon amines.

(4) By the reduction of their oxidation products.

From nucleus-syntheses (p. 85):

(5) By the action of zinc alkyls, or zinc alkyls and alkyl iodides, upon aldehydes, acid chlorides, ketones, formic esters, acetic esters, and chlorinated ethers.

(1*a*) *From Haloid Esters or Alkylogens.*—It was mentioned, in describing the transformations of the alkylogens, that the latter afford a means of passing from the paraffins and olefines to the alcohols (p. 101). As caustic alkali causes the separation of a halogen hydride from the alkylogens, it is possible to exchange hydroxyl for the halogen, especially if this be iodine. This is most easily accomplished by the action of freshly precipitated, moist silver oxide, or by heating with lead oxide and water:

$$C_2H_5I + AgOH = C_2H_5 . OH + AgI.$$

Even water alone causes a partial transposition of the more reactive tertiary alkyl iodides; whereas the other alkylogens in general when heated for some time with 10–15 volumes of water to 100° are completely converted into alcohols (A. **186**, 390).

Tertiary alkyl iodides heated to 100° with methyl alcohol pass into methyl alcohols and methyl iodide (A. **220**, 158).

(1*b*) *By the Saponification of their Esters.*—It is often more practical to first convert the halogen derivatives into acetic acid esters, by heating with silver or potassium acetate:

$$C_2H_5Br + \underset{\text{Potassium Acetate.}}{C_2H_3O . OK} = \underset{\text{Ethyl Acetic Ester.}}{C_2H_5 . O . C_2H_3O} + KBr,$$

and then boil these with potassium or sodium hydroxide, and obtain the alcohols:

$$C_2H_5 . O . C_2H_3O + KOH = C_2H_5 . OH + C_2H_3O . OK.$$

The second reaction is called *saponification*, because by means of it the soaps, *i. e.*, the alkali salts of the fatty acids and glycerol (see this), are obtained from the glycerol esters of the fatty acids—the fats.

(1*c*) By decomposing the acid esters of sulphuric acid with boiling water:

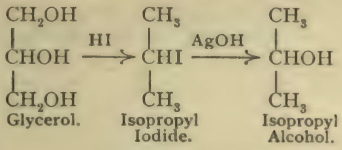
$$SO_2{<}{\begin{matrix} O . C_2H_5 \\ OH \end{matrix}} + H_2O = C_2H_5 . OH + SO_4H_2.$$

Ethyl Sulphuric Acid.

This reaction constitutes the transition from the olefines to the alcohols, as these esters may be easily obtained by directly combining the unsaturated hydrocarbons with sulphuric acid.

Many alkylens (like iso- and pseudo-butylene) dissolve at once in dilute nitric acid, absorb water, and yield alcohols (A. **180**, 245).

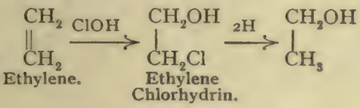
(2) *The reduction of polyhydric alcohols* by hydriodic acid yields the iodides of secondary alcohols, which are converted by methods 1*a* and 1*b* into the alcohols themselves, *e. g.*:



$$\begin{matrix} CH_2OH & & CH_3 & & CH_3 \\ | & & | & & | \\ CHOH & \xrightarrow{HI} & CHI & \xrightarrow{AgOH} & CHOH \\ | & & | & & | \\ CH_2OH & & CH_3 & & CH_3 \end{matrix}$$

Glycerol. Isopropyl Iodide. Isopropyl Alcohol.

Or, the chlorhydrins of the polyhydric alcohols may be reduced, *e. g.*:



$$\begin{matrix} CH_2 & & CH_2OH & & CH_2OH \\ \| & \xrightarrow{ClOH} & | & \xrightarrow{2H} & | \\ CH_2 & & CH_2Cl & & CH_3 \end{matrix}$$

Ethylene. Ethylene Chlorhydrin.

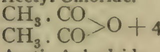
(3) *Action of nitrous acid upon the primary amines:*

$$C_2H_5NH_2 + NO.OH = C_2H_5.OH + N_2 + H_2O.$$

Very often transpositions occur with the higher alkylamines, and instead of the primary alcohols, we obtain secondary alcohols (B. **16**, 744).

(4*a*) Primary alcohols result from the reduction of *aldehydes, acid chlorides*, and *acid anhydrides:*

$C_2H_5.COH + 2H = CH_3.CH_2.CH_2.OH$ (Würtz, A. **123**, 140).
Propyl Aldehyde.
$CH_3.COCl + 4H = CH_3.CH_2.OH + HCl$.
Acetyl Chloride.



$\begin{matrix} CH_3.CO \\ CH_3.CO \end{matrix}\!>\!O + 4H = C_2H_5.OH + CH_3.COOH$ (Linnemann, A. **148**, 249).
Acetic Anhydride.

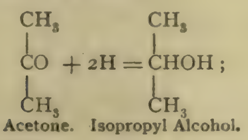
Aldehydes are first formed in the reduction of acid chlorides and anhydrides; they in turn are reduced to alcohols. The reducing agents are dilute sulphuric acid or acetic acid, together with sodium amalgam, sodium, iron filings, and zinc dust (B. **9**, 1312; **16**, 1715).

This is the last of those reactions by which an alcohol can be converted into another, containing an atom more of carbon. The alcohol is changed through the iodide to the cyanide, and the latter to the acid, which, by reduction of its chloride or its aldehyde, yields the new alcohol:

$$CH_3.OH \longrightarrow CH_3I \longrightarrow CH_3CN \longrightarrow CH_3.COOH \longrightarrow CH_3COC$$

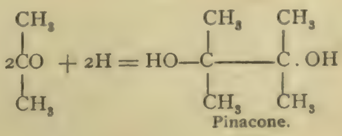
$$CH_3.CH_2OH \longleftarrow$$

(4*b*) *The reduction of ketones* yields *secondary alcohols* (Friedel, A. **124**, 324), together with pinacones (see these), the di-tertiary dihydric alcohols or glycols:



$$\begin{matrix} CH_3 & & CH_3 \\ | & & | \\ CO & + 2H = & CHOH; \\ | & & | \\ CH_3 & & CH_3 \end{matrix}$$

Acetone. Isopropyl Alcohol.



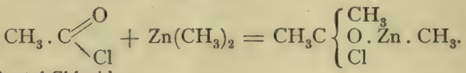
$$\begin{matrix} CH_3 & & & CH_3 & & CH_3 \\ | & & & | & & | \\ 2CO & + 2H = & HO- & C & - & C.OH \\ | & & & | & & | \\ CH_3 & & & CH_3 & & CH_3 \end{matrix}$$

Pinacone.

Nucleus-synthetic Methods of Formation.

(5*a*) *Acid Chlorides and Zinc Alkyls; Ketones, Zinc Alkyls and Alkylogens.*—A very remarkable synthetic method, proposed by Butlerow (1864), which led to the discovery of the **tertiary** alcohols, consists in the action of the zinc compounds of the alkyls upon the chlorides of the acid radicals (Z. f. Ch., 1864, 385; 1865, 614).

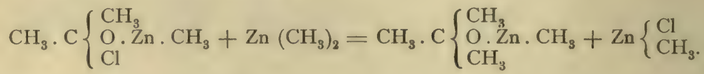
The reaction divides itself into three phases. At first only one molecule of zinc alkyl reacts, and adds itself to the acid chloride as a result of the breaking down of the double linkage between the carbon and oxygen:

(1) 

$$CH_3.C\genfrac{}{}{0pt}{}{\diagup\!\!\diagup O}{\diagdown Cl} + Zn(CH_3)_2 = CH_3C\begin{cases}CH_3\\ O.Zn.CH_3.\\ Cl\end{cases}$$

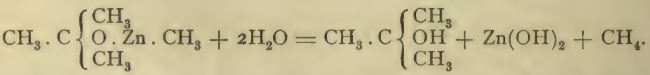
Acetyl Chloride.

By decomposing the reaction-product with water, acetone is formed. However, should a second molecule of the zinc alkyl act upon the new compound, further reaction will take place on longer standing:

(2) 

$$CH_3.C\begin{cases}CH_3\\ O.Zn.CH_3\\ Cl\end{cases} + Zn\ (CH_3)_2 = CH_3.C\begin{cases}CH_3\\ O.Zn.CH_3\\ CH_3\end{cases} + Zn\begin{cases}Cl\\ CH_3.\end{cases}$$

If now water be permitted to take part, a tertiary alcohol will be formed:

(3) 

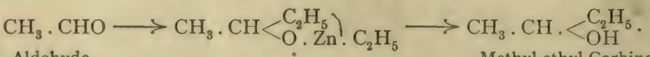
$$CH_3.C\begin{cases}CH_3\\ O.Zn.CH_3\\ CH_3\end{cases} + 2H_2O = CH_3.C\begin{cases}CH_3\\ OH\\ CH_3\end{cases} + Zn(OH)_2 + CH_4.$$

If in the second stage the zinc compound of another radical be employed, the latter may be introduced, and in this manner we obtain tertiary alcohols with two or three different alkyls (A. **175**, 374, and **188**, **110**, **122**).

It is remarkable that only zinc methyl and ethyl furnish tertiary alcohols, while zinc propyl affords only those of the secondary type (B. **16**, 2284; **24**, R. 667).

The *ketones* in general do not react with the zinc alkyls. On the other hand, diethyl-acetone, $(C_2H_5)_2CO$, and dipropyl ketone, $(C_3H_7)_2CO$, are converted by zinc and methyl (ethyl) iodide into zinc alkyl compounds; these, under the influence of water, pass into *tertiary* alcohols (B. **19**, 60; **21**, R. 55). We get unsaturated tertiary alcohols from all the ketones by the action of zinc and allyl iodide (A. **196**, 113).

(5*b*) When zinc alkyls act upon aldehydes, only one alkyl group enters, and the reaction product of the first stage yields a *secondary* alcohol when treated with water (A. **213**, 369; and B. **14**, 2557):

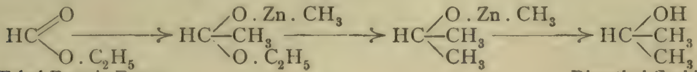


$$CH_3.CHO \longrightarrow CH_3.CH<\begin{matrix}C_2H_5\\ O.Zn.C_2H_5\end{matrix} \longrightarrow CH_3.CH.<\begin{matrix}C_2H_5\\ OH\end{matrix}.$$

Aldehyde. Methyl-ethyl Carbinol.

All aldehydes (even those with unsaturated alkyls, and also furfuran) react in this way—but only with zinc methyl and zinc ethyl, while with the higher zinc alkyls the aldehydes suffer reduction to their corresponding alcohols (B. **17**, R. 318). With zinc methyl chloral yields trichlorisopropyl alcohol, $CCl_3.CH(OH).CH_3$; whereas with zinc ethyl it is only reduced to trichlorethyl alcohol (A. **223**, 162).

(5*c*) Just as we obtained tertiary alcohols from the acid radicals, so can we derive *secondary alcohols* from the esters of formic acid. Zinc alkyls are allowed to react in this case (or, better, alkyl iodides and zinc), and two alkyls are introduced:



Ethyl Formic Ester. Dimethyl Carbinol.

Using some other zinc alkyl in the second stage of the reaction, or by working with a mixture of two alkyl iodides and zinc, two different alkyls may also be introduced here (A. **175**, 362, 374).

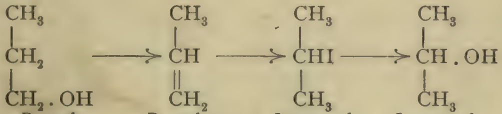
Zinc and allyl iodide (not ethyl-iodide, however) react similarly upon acetic acid esters. Two alkyl groups are introduced and unsaturated tertiary alcohols formed (A. **185**, 175).

Chlorinated ethers, *e. g.*, $ClCH_2 . OCH_3$, and zinc alkyls yield ethers of primary alcohols (B. **24**, R. 858):

$$2Cl . CH_2 . OCH_3 + Zn(C_2H_5)_2 = 2C_2H_5 . CH_2 . OCH_3 + ZnCl_2.$$

In addition to the above universal methods, alcohols are formed by various other reactions. Their formation in the alcoholic fermentation of sugars in the presence of ferments is of great practical importance. Appreciable quantities of methyl alcohol are produced in the dry distillation of wood. Many alcohols, too, exist as already formed natural products in compounds, chiefly as compound ethers of organic acids.

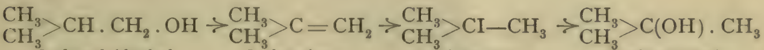
Conversion of Primary into Secondary and Tertiary Alcohols.—By the elimination of water the primary alcohols become unsaturated hydrocarbons C_nH_{2n} (p. 91). The latter, treated with concentrated HI, yield iodides of secondary alcoholic radicals, as iodine does not attach itself to the terminal but to the less hydrogenized carbon atom (p. 93). Secondary alcohols appear when these iodides are acted upon with silver oxide. The successive conversion is illustrated in the following formulas:



$$\begin{array}{c}CH_3\\|\\CH_2\\|\\CH_2 . OH\end{array} \longrightarrow \begin{array}{c}CH_3\\|\\CH\\\|\\CH_2\end{array} \longrightarrow \begin{array}{c}CH_3\\|\\CHI\\|\\CH_3\end{array} \longrightarrow \begin{array}{c}CH_3\\|\\CH . OH\\|\\CH_3\end{array}$$

Propyl Alcohol. Propylene. Isopropyl Iodide. Isopropyl Alcohol.

Primary alcohols in which the group $CH_2.OH$ is joined to a secondary radical, pass in the same manner into tertiary alcohols:



$$\begin{array}{l}CH_3\\CH_3\end{array}\!\!>CH . CH_2 . OH \rightarrow \begin{array}{l}CH_3\\CH_3\end{array}\!\!>C=CH_2 \rightarrow \begin{array}{l}CH_3\\CH_3\end{array}\!\!>CI—CH_3 \rightarrow \begin{array}{l}CH_3\\CH_3\end{array}\!\!>C(OH) . CH_3$$

Isobutyl Alcohol. Isobutylene. Tertiary Butyl Iodide. Tertiary Butyl Alcohol.

The change is better effected by the aid of sulphuric acid. The sulphuric esters (p. 93), arising from the alkylens, C_nH_{2n}, have the sulphuric acid residue linked to the carbon atom, with the least number of attached hydrogen atoms.

Physical Properties.—In physical properties alcohols exhibit a gradation corresponding to their increase in molecular weight. This is true of other bodies belonging to homologous series. The lower alcohols are mobile liquids, dissolving readily in water, and possessing the characteristic alcohol odor and burning taste. As their carbon content increases, their solubility in water grows rapidly less. The normal alcohols, containing from one to sixteen carbon atoms, are oils at the ordinary temperature, while the higher are crystalline solids, without odor or taste. They resemble the fats. Their boiling points increase gradually (with similar structure) in proportion to the increase of their molecular weights. This is about 10° for the difference, CH_2. The primary alcohols boil higher than the isomeric secondary, and the latter higher than the tertiary. Here we observe again that the boiling points are lowered with the accumulation of methyl groups (see p. 64). The boiling points can be calculated with approximate accuracy from the alkyl residues present (B. **20**, 1948). The higher members are only volatile without decomposition under diminished pressure.

Chemical Properties and Transpositions.—The alcohols are neutral compounds. In many respects the first members of the series resemble water, and enter into combination with many salts, in which they play the rôle of water of crystallization (p. 118).

Some of their more important transpositions are—

(1) The hydroxyl hydrogen is easily replaced by sodium, potassium, and other metals, yielding thereby the *alcoholates*.

(2) In their interaction with strong acids water separates and *compound ethers* or *esters* are produced. This reaction is analogous to that taking place in the formation of a salt from a basic oxyhydrate and an acid. The alcohols figure as the base (p. 132).

(3) The *haloid esters* of the alcohols are produced when the alcohols are heated together with the haloid acids. These esters are the monohalogen derivatives of the paraffins (p. 101). A more convenient method for their formation consists in heating the alcohols with the phosphorus haloids.

Nascent hydrogen, acting upon these esters, affords a means of reconverting the alcohols into their corresponding hydrocarbons (p. 101).

(4) Energetic dehydrating agents change the alcohols, especially those of the tertiary class, into the olefines (p. 92).

(5) Heated with phenols and zinc chloride, they yield homologous phenols (see these).

Reactions, Distinguishing Primary, Secondary, and Tertiary Alcohols.—(1) In the preliminary description of the alcohols it was clearly shown that primary alcohols, upon oxidation, yield aldehydes and carboxylic acids; that the secondary alcohols form ketones with like carbon-content (p. 111), and that the tertiary alcohols break down.

(2) If the alcohols be converted by phosphorus iodide (p. 100) into their iodides, and the latter are changed by silver nitrite to nitroalkyls (see these), the latter com-

pounds will show characteristic color reactions, according as they contain a primary, secondary, or tertiary alcohol radical.

(3) Acetic esters are formed when the primary and secondary alcohols are heated with acetic acid to 155° C. The tertiary alcohols, under similar treatment, split off water and form alkylens (A. **190**, 343; **197**, 193; **220**, 165).

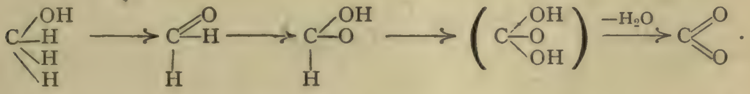
(4) When the primary alcohols are heated together with soda-lime they yield their corresponding acids:

$$R.CH_2.OH + NaOH = R.CO.ONa + 2H_2.$$

A. LIMIT-ALCOHOLS, PARAFFIN ALCOHOLS, $C_nH_{2n+1}OH$.

The most important members of this series, and of the monohydric alcohols in particular, are *methyl alcohol* or *wood spirit*, $CH_3.OH$, and *ethyl alcohol* or *spirits of wine:* $CH_3.CH_2.OH$.

1. Methyl Alcohol, *Wood Spirit*, *Carbinol* [*Methanol*], $CH_3.OH$, differs from all other primary alcohols in that it contains the CH_2OH group in union with hydrogen. Hence its oxidation is not restricted to the corresponding monobasic carboxylic acid, but may extend to carbonic acid:



It is formed in large amounts in the dry distillation of wood. The name methyl, derived from μέθυ, wine, and ὕλη, wood, is a translation of wood spirit.

History.—Boyle discovered wood spirit in 1661 among the dry distillation products of wood. In 1812 Taylor recognized it as similar to spirits of wine, but considered it an entirely different body. Dumas and Péligot (1831) (A. **15**, 1) made the first careful study of it.

Methyl alcohol is also produced in the dry distillation of molasses. It occurs in nature as methyl salicylic ester, $C_6H_4\left\{\begin{matrix}[1]COOCH_3\\ [2]OH\end{matrix}\right.$, *wintergreen oil*, derived from *Gaultheria procumbens*.

The full synthesis of methyl alcohol proceeds from carbon disulphide through methane, and methyl chloride, by action of aqueous caustic potash on the latter at 100° (Berthelot, 1858, A. chim. phys. [3] **52**, 101):

$$CS_2 \longrightarrow CH_4 \longrightarrow CH_3Cl \xrightarrow{KOH} CH_3.OH.$$

Physical Properties.—Methyl alcohol is a mobile liquid with spirituous odor and burning taste. It boils under 760 mm. at 66–67°, and at 20° it has a specific gravity of 0.796. It mixes with water, alcohol, and ether.

The aqueous product obtained in the distillation of wood at 500° in iron retorts contains methyl alcohol, acetone, acetic acid, methyl acetic ester, and other compounds. It is distilled over burnt lime or soda. The crude wood spirit which results contains acetone as its chief impurity. To remove this add anhydrous calcium chloride. The latter combines with the alcohol to a crystalline compound. This is removed, freed from acetone by distillation, and afterward decomposed by distilling with water. Pure aqueous methyl alcohol passes over; this is dehydrated with lime or potashes. To procure it perfectly pure it is only necessary to break up oxalic methyl ester, the high-boiling methyl benzoate, or methyl acetic ester, with caustic potash.

To detect ethyl in methyl alcohol, heat the latter with concentrated sulphuric acid, when acetylene will be formed from the first. Under this treatment methyl alcohol becomes methyl ether. The amount of methyl alcohol in wood spirit is determined, quantitatively, by converting it into methyl iodide, CH_3I, through the agency of PI_3 (B. **9**, 1928). We estimate the quantity of acetone by the iodoform reaction (B. **13**, 1000).

Uses.—Wood spirit is employed as a source of heat. It is also used in making varnishes, dimethylaniline, and for the methylation of many carbon derivatives, particularly the dye-stuffs. It is a good solvent for many compounds of carbon.

Chemical Properties.—(1) It combines directly with $CaCl_2$, to form $CaCl_2 . 4CH_4O$, crystallizing in brilliant six-sided plates. Barium oxide dissolves in methyl alcohol, forming the crystalline body $BaO . 2CH_4O$. The alcohol in this salt conducts itself like *water of crystallization.*

(2) Potassium and sodium dissolve in anhydrous alcohol, to form methylates, *e. g.*, CH_3OK and $CH_3 . ONa$.

(3) Oxidizing agents and also air, in presence of platinum black, change methyl alcohol to formic aldehyde, formic acid, and carbonic acid.

(4) Chlorine and bromine do not act so readily upon methyl as upon ethyl alcohol. Chlorine attacks aqueous methyl alcohol quite easily (B. **28**, R. 771). Dichlormethyl ether, $(ClCH_2)_2O$, is first produced; water converts it into formaldehyde and hydrochloric acid (B. **26**, 268).

(5) When methyl alcohol is heated with soda-lime, sodium formate results:

$$CH_3 . OH + NaOH = CHO . ONa + 2H_2.$$

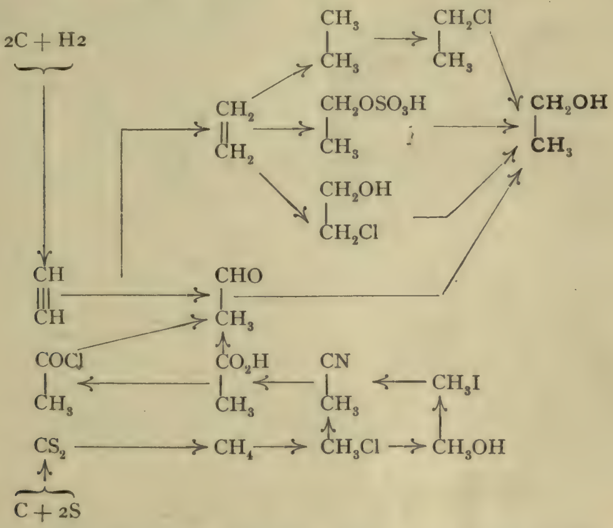
(6) When the alcohol is distilled over zinc dust, it breaks down into carbon monoxide and water.

2. Ethyl Alcohol, *Spirits of Wine* [*Ethanol*], $C_2H_5 . OH$.—In consequence of its formation in the spirituous fermentation of saccharine plant juices, alcohol, in impure state, was known to the ancients. It was, however, only in the preceding century that the knowledge of how it might be obtained in an anhydrous condition was acquired. In 1808 Saussure determined its constitution.

Occurrence.—Ethyl alcohol seldom occurs in the vegetable kingdom. It is found, together with ethyl butyrate, in the unripe seeds of *Heracleum giganteum* and *Heracleum spondylium.* It is also present in the urine of diabetic patients, and in that of healthy men after excessive consumption of alcoholic beverages.

Formation.—It may be obtained by the general methods previously described for primary alcohols: (1) From ethyl chloride; (2) from ethyl sulphate; (3) from ethylene chlorhydrin; (4) from ethylamine;

(5) from aldehyde; and (6) from acetyl chloride. The synthesis of ethyl alcohol is, therefore, possible in two ways. The first three methods show that it is genetically connected with acetylene, ethylene, and ethane, while the last two methods indicate its relation to acetylene and acetic acid (p. 112):



Starting with acetylene, the most direct course to ethyl alcohol would be through acetaldehyde. Water converts it into the latter (p. 96), and nascent hydrogen then reduces the aldehyde to alcohol.

If the acetylene be changed to ethylene, then various possibilities arise for the formation of ethyl alcohol: (1) Ethylene and hydrogen unite to form ethane, which chlorine changes to ethyl chloride, yielding alcohol when heated with water. (2) At 160° ethylene unites with sulphuric acid, forming ethyl sulphuric acid, which boiling water changes to ethyl alcohol and sulphuric acid. (3) Ethylene and hypochlorous acid yield ethylene chlorhydrin, which may be reduced to ethyl alcohol.

A nucleus-synthesis of ethyl alcohol from methyl alcohol is possible through acetaldehyde. Methyl alcohol can be synthesized from carbon disulphide (p. 117). Phosphorus iodide converts the methyl alcohol into methyl iodide, and this, by action of potassium cyanide, is changed into methyl cyanide. Boiling alkali transforms the latter into an alkaline acetate, which phosphorus oxychloride converts into acetyl chloride. The latter, by reduction, yields ethyl alcohol, with acetaldehyde as an intermediate product. Acetaldehyde may also be prepared from calcium acetate by heating it with calcium formate.

Preparation.—Ethyl alcohol is prepared on a technical scale almost exclusively by what is termed the "spirituous fermentation" of saccharine juices.

Cagniard Latour, in 1836, and later Schwann, found that alcoholic fermentation was due to yeast germs—an organized ferment (A. 29, 100; 30, 250, 363; A. chim. phys. [3], 58, 323). [These broke down the various sugars into alcohol and carbon dioxide. Yeast consists of microscopic cells (about 0.01 mm. in size): *saccharomyces cerevisiæ seu vini.*

Conditions of Alcoholic Fermentation.—The yeast germs increase by budding. This takes place in dilute, warm (5–30°) sugar solutions. It is most rapid at 20–30° C. The growth requires salts, especially phosphates, and albuminous substances. Oxygen is requisite at the commencement (B. **29**, 1983), but the fermentation proceeds afterward without air access. If the quantity of alcohol in a fermenting liquid reaches a certain amount, the fermentation ceases. The yeast germs can not grow in liquids containing 14 per cent. of alcohol. They are also destroyed by a temperature of 60°, and by small quantities of phenol, salicylic acid, corrosive sublimate, and other disinfectants.

The sugars occurring in ripening fruits—grapes, apples, cherries—and in cane and beet sugars, as well as in many other plants, are the *carbohydrates*, which contain hydrogen and oxygen together with carbon in the same proportion in which the first two elements are present in water. The carbohydrates will be discussed immediately after the hexahydric alcohols: $C_6H_8(OH)_6$—*mannitol, dulcitol, sorbitol*, etc., whose first oxidation products are the simple carbohydrates, $C_6H_{12}O_6$. However, so much relating to the carbohydrates will be given at this time as appears necessary to understand alcoholic fermentation.

The carbohydrates may be arranged into three principal classes:

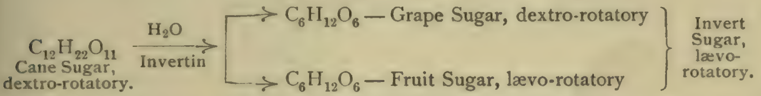
1. *Glucoses* or *Monoses*, $C_6H_{12}O_6$: grape sugar, fruit sugar, etc.
2. *Saccharobioses*, $C_{12}H_{22}O_{11}$: malt sugar, cane sugar, milk sugar, etc.
3. *Polysaccharides*, $(C_6H_{10}O_5)x$: starch, dextrine, etc.

The carbohydrates of the second and third classes bear the relation of *anhydrides* to the sugars of the first group.

The simple sugars of the formula $C_6H_{12}O_6$ are capable of direct alcoholic fermentation. This is particularly true of *grape* and *fruit* sugar, as well as of *malt* sugar among the saccharobioses. Technically, it is of the greatest importance that the *not* directly fermentable saccharobioses and the polysaccharides can be converted by water absorption into directly fermentable sugars, and these then be fermented.

Unorganized Ferments or Enzymes.—The breaking-down of saccharobioses and polysaccharides by water absorption (*by hydrolysis*) is induced by enzymes—albuminoid-like compounds. The most important of this class are *invertin* and *diastase.*

Invertin is produced in the yeast germ. It is soluble in water and has acquired its name from the fact that it is capable of converting cane sugar into equimolecular quantities of grape sugar and fruit sugar—so called *invert sugar.* At the same time the rotatory power of the liquid is reversed—it is *inverted.* Cane sugar is dextro-rotatory. This is also true of grape sugar, whereas fruit sugar deviates the plane of polarized light more strongly toward the left, than an equivalent quantity of grape sugar turns it to the right. Consequently, inversion changes a dextro-rotatory cane-sugar solution into a lævo-rotatory solution of invert sugar:

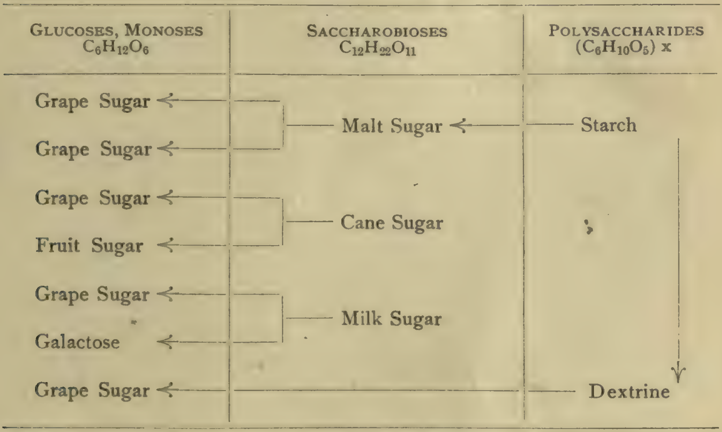


$$\underset{\substack{\text{Cane Sugar,}\\\text{dextro-rotatory.}}}{C_{12}H_{22}O_{11}} \xrightarrow[\text{Invertin}]{H_2O} \left[\begin{array}{l} \to C_6H_{12}O_6 \text{ — Grape Sugar, dextro-rotatory} \\ \\ \to C_6H_{12}O_6 \text{ — Fruit Sugar, lævo-rotatory}\end{array}\right\} \begin{array}{c}\text{Invert}\\\text{Sugar,}\\\text{lævo-}\\\text{rotatory.}\end{array}$$

Diastase is an unorganized ferment, produced in the germination of barley and other grains. The germination of the so-called *green malt* is interrupted by killing the germ by rapid drying. The *malt* is then subjected to kiln-drying, a temperature which will not influence the activity of the diastase. At 50° to 60° the diastase in malt can hydrolyze the starch. Two-thirds of the latter are changed to *malt sugar*, which can be directly fermented by yeast. One-third of the starch becomes *dextrine*. This is converted much more slowly by the diastase into grape sugar.

Malt sugar, like grape sugar, belongs to the saccharobioses. It absorbs water and is resolved into grape sugar. Milk sugar, also a saccharobiose, absorbs water and passes into a mixture of equimolecular quantities of galactose and grape sugar. A review of these hydrolytic relations is shown in the following diagram:

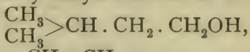
CARBOHYDRATES.



The hydrolysis of the saccharobioses and of starch may also be brought about by warm, dilute sulphuric acid. This treatment changes the starch to grape sugar and dextrine. In technical operations the preparation of saccharine juices from starchy compounds for the purpose of fermentation is executed almost exclusively by the diastase of malt.

Pasteur considers that from 94 to 95 per cent. of sugar changes to *alcohol* and *carbonic acid* according to the equation:

$$C_6H_{12}O_6 = 2C_2H_6O + 2CO_2.$$

Fusel oil, some *glycerol* (2–5 per cent.) and *succinic acid* (0.6 per cent.) are formed simultaneously, although the latter two appear generally toward the end of the fermentation (B. **27**, R. 671). The fusel oil contains n-propyl alcohol, isopropyl alcohol, isobutyl alcohol $(CH_3)_2CH.CH_2OH$, and especially amyl alcohol of fermentation—a mixture of isobutyl carbinol,  $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH.CH_2.CH_2OH$, and optically active methyl-ethyl-carbin-carbinol,  $\begin{matrix}CH_3.CH_2\\CH_3\end{matrix}\!\!>{}^*CH.CH_2.OH$ (p. 128).

Not only the varieties of saccharomyces, but also other budding fungi, *e. g.*, *Mucor mucedo*, induce alcoholic fermentation. The various secondary fermentations occasioned by *schizomycetes* are remarkable. It appears that the fusel oil is produced by them in ordinary yeast fermentations. Alcoholic fermentation occurs without the agency of organisms in unimpaired ripe fruits (grapes and cherries), when these are exposed for a period in an atmosphere of carbon dioxide.

Alcoholic Beverages.—The material used in the preparation of alcoholic liquids by means of fermentation are:

1. *Saccharine plant juices.*

2. *Starch-containing substances*, seeds of grain and potatoes. The fermented liquids are directly consumed (*wine*, *beer*) or they are first distilled in order to produce the various kinds of *brandy*, the alcohol content of which may exceed 50 per cent.:

(1) By the fermentation of saccharine juices we obtain:

(*a*) *without* subsequent distillation:	(*b*) *with* subsequent distillation:
From grapes: wine.	From wine: cognac.
" apples: cider.	" molasses: rum.
" St. John's berries: wine, etc.	" cherries: cherry water.
	" prunes: sliwowitz (Bohemia), etc.

(2) By the fermentation of starch-containing substances, after converting the starch into sugar with malt:

(*a*) *without* subsequent distillation:	(*b*) *with* subsequent distillation:
Barley: beer.	Barley and rye, wheat or oats, and maize: corn whiskey of various kinds.
Wheat: weiss-beer (Berlin).	Rice: arrac (East India).
	Potatoes: potato spirit.

*Manufacture of Potato Spirit.**—Pure ethyl alcohol is obtained from potato spirit. At first the potatoes are heated with steam to 140–150° C. under a pressure of from 2–3 atmospheres. The lower part of the apparatus is now opened and the potato mash pressed out and digested at 57–60° in a mashing apparatus with finely divided malt containing water. In this manner the starch of the potatoes is converted into sugar. When the *mash* has cooled to the temperature of fermentation it is run into the fermentation-tubs, where it comes in contact with "pure culture" artificial yeast, and is then fermented. *Crude spirit* results from the distillation of the fermented mash. What remains is the vinasse.

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* Ferd. Fischer: Hdb. d. chem. Technologie, 14. Aufl., 1893, S. 948.

Manufacture of Pure, Absolute Alcohol.—To further purify the crude spirit it is fractionated on a large scale in the column apparatus of Savalle, Pistorius, Ilges.* The first portions, more readily volatile, contain aldehyde, acetal, and other substances. A purer spirit (containing 95–96 per cent. of alcohol) follows, and in commerce is known as *sprit.* Finally come the *tailings*, in which are the fusel oils. To remove the latter, the spirit is diluted with water and filtered through ignited wood-charcoal, which retains the fusel oils, and is then distilled.

To prepare anhydrous alcohol, the rectified spirit (90–95 per cent. alcohol) is distilled with ignited potashes, anhydrous copper sulphate, caustic lime (A. **160**, 249), or barium oxide.

Detection of Water in Alcohol.—Absolute alcohol dissolves barium oxide, assuming a yellow color at the same time. **1.** It is soluble without turbidity in a little benzene; when more than three per cent. water is present, cloudiness ensues. **2.** On adding anhydrous or absolute alcohol to a mixture of very little anthraquinone and some sodium amalgam it becomes dark green in color, but in the presence of traces of water a red coloration appears (B. **10**, 927).

Detection of Alcohol.—Traces of alcohol in solutions are detected and determined either by oxidation to aldehyde (see this) or by converting it by means of dilute potash and iodine into iodoform (B. **13**, 1002).

Its conversion into ethyl benzoate, by shaking with benzoyl chloride and sodium hydroxide (B. **19**, 3218; **21**, 2744) also answers for this purpose.

Properties.—Absolutely pure alcohol is a mobile, colorless liquid with an agreeable ethereal odor, boils at 78.3° (760 mm.), and has a specific gravity of 0.80625 at 0°, or 0.78945 at 20°. At —90° it is a thick liquid, at—130° it solidifies to a white mass. It burns with a non-luminous flame and absorbs water energetically from the air. When mixed with water a contraction occurs, accompanied by rise of temperature; the maximum is reached when one molecule of alcohol is mixed with three molecules of water, corresponding to the formula $C_2H_6O + 3H_2O$. The amount of alcohol in aqueous solutions is given either in per cents. by weight (degrees according to Richter) or volume per cents. (degrees according to Tralles). It may be determined by an *alcoholometer*, the scale of which gives directly the per cent. by weight or volume for a definite temperature (15° C.). Or the vapor tension is ascertained by means of the *vaporimeter* of Geissler, or the boiling point is determined with the *ebullioscope.*

The alcohol content of spirituous drinks is first distilled off and then estimated.†

Alcohol dissolves many mineral salts, the alkalies, hydrocarbons, resins, fatty acids, and almost all the carbon derivatives. The most of the gases are more readily soluble in it than in water; 100 volumes of alcohol dissolve 7 volumes of hydrogen, 25 volumes of oxygen, and 16 volumes of nitrogen.

Ethyl alcohol forms crystalline compounds with some salts, like cal-

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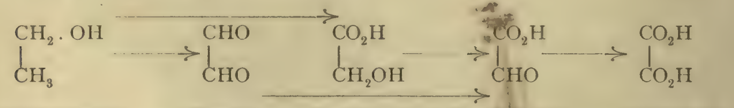
* Ferd. Fischer: Hdb. d. chem. Technologie, 14. Aufl., 1893, S. 959.

† Post: Chemisch-technische Analyse, Braunschweig, 1881; Böckmann, Chem.-tech. Untersuchungsmethoden, Berlin, 1888; König: Chemie der menschlichen Nahrungs und Genussmittel, 1893; Elsner: Die Praxis des Chemikers bei Untersuchung von Nahrungsmitteln, etc., 1893.

cium chloride and magnesium chloride. It plays the rôle of water of crystallization in them.

Transpositions.—Potassium and sodium dissolve in it, yielding the alcoholates.

With sulphuric acid it yields ethyl sulphuric acid, and with sulphuric anhydride, carbyl sulphate (p. 91). Phosphorus bromide and iodide change it into ethyl bromide and ethyl iodide. Being a primary alcohol, such oxidants as manganese peroxide and sulphuric acid, chromic acid, platinum black, and air change it to acetaldehyde and acetic acid (p. 111). Chlorine and bromine oxidize alcohol to acetaldehyde, which unites to *acetal* with the alcohol. Chloral- and bromal-alcoholates are derived from acetal. Bleaching lime changes alcohol to chloroform, and iodine and caustic potash convert it into iodoform. Nitric acid, free from nitrous acid, changes alcohol into ethyl nitrate (see this). Under certain conditions alcohol can be so oxidized by nitric acid that, besides attacking the $CH_2 . OH$ group, the methyl-group may be changed with the resulting formation of glyoxal, glycollic acid, glyoxalic acid, and oxalic acid:



Ethyl Alcohol. Glyoxal. Glycollic Acid. Glyoxalic Acid. Oxalic Acid.

Fulminating mercury (see this) is produced when alcohol acts upon mercury and an excess of nitric acid.

Alcoholates.—Sodium ethylate is the most important alcoholate, as it has been applied in a series of nucleus-synthetic reactions. It affords a means of splitting off water and alcohol. It may be made by dissolving sodium in alcohol, then heating it to 200° C. in an atmosphere of hydrogen to free it from alcohol. It is a white, voluminous powder (A. **202**, 294; B. **22**, 1010). Or a calculated quantity of metallic sodium is added to toluene or xylene containing alcohol, and the whole heated with a return cooler until the sodium has entirely disappeared (B. **24**, 649). An excess of water changes the alcoholates to alcohol and sodium hydroxide. The transposition is very slight with a small amount of water. Hence the alcoholates result on dissolving KOH and NaOH in strong alcohol. Sodium peroxide converts alcohol into sodium alcoholate and natryl hydroxide, $NaO . OH$ (B. **27**, 2299).

Calcium Ethylate, $Ca(OC_2H_5)_2$, is formed by the decomposition of calcium carbide by alcohol (B. **28**, R. 61).

Aluminium Ethylate, $Al(OC_2H_5)_3$, is rather interesting, in that it volatilizes without decomposition under much reduced pressure.

Substituted Ethyl Alcohols:

1.	$CH_2Cl . CH_2OH$	Glycol Chlorhydrin (Bromhydrin, Iodhydrin).
2.	$CHCl_2 . CH_2OH$	Dichlorethyl Alcohol, liquid with B. P 146° (B. **20**, R. 363).
3.	$CCl_3 . CH_2OH$	Trichlorethyl Alcohol, melts at 18°; boils at 151° (A. **210**, 63).
4.	$CH_2NO_2 . CH_2OH$	Nitroethyl Alcohol.
5.	$CH_2 . NH_2 . CH_2OH$	Oxethylamine, } Amidoethyl Alcohols.
6.	$CH_3 . CH(NH_2)OH$	Aldehyde Ammonia, } Amidoethyl Alcohols.

The compounds 1, 2, and 5 will be taken up together with ethylene glycol, and 6 with acetaldehyde. Di- and trichlorethyl alcohols have been prepared by the interaction of zinc ethide and di- and trichloracetaldehyde (p. 114), while trichlorethyl alcohol is formed from urochloralic acid (see this). The connection between the chlorinated ethyl alcohols and their oxygen compounds, whose chlorides they may be assumed to be, is seen in the following tabulation:

Monochlorethyl Alcohol, $CH_2Cl.CH_2OH$, corresponds to $CH_2 . OH . CH_2OH$—Glycol.
Dichlorethyl Alcohol, $CHCl_2 . CH_2OH$, corresponds to $CHO . CH_2OH$—Glycolyl Aldehyde.
Trichlorethyl Alcohol, $CCl_3 . CH_2OH$, corresponds to $COOH . CH_2OH$–Glycollic Acid.

3. **Propyl Alcohols** [*Propanols*], $C_3H_7 . OH$.—As explained in the introduction to the monohydric alcohols, two isomeric propyl alcohols are theoretically possible: normal propyl alcohol and secondary isopropyl alcohol. Their constitution is evident from their methods of formation and their transpositions (p. 115).

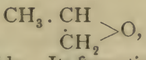
Normal propyl alcohol, $CH_3 . CH_2 . CH_2 . OH$, boils at 97.4°; sp. gr., 0.8044 at 20°.

Isopropyl alcohol, $CH_3 . CH(OH)—CH_3$, boils at 82.7°; sp. gr., 0.7887 at 20°.

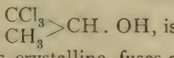
Normal Propyl Alcohol may be obtained from fusel oil (Chancel, 1853) by fractional distillation. It is an agreeable-smelling liquid. It is miscible in every proportion with water, but is insoluble in a saturated, cold calcium chloride solution, and this distinguishes it from ethyl alcohol. It may be artificially prepared from propyl aldehyde and by action of nascent hydrogen.

It passes into propionic aldehyde and propionic acid, under the influence of oxidizing agents. When heated with H_2SO_4 it yields propylene, which hydrogen iodide changes to isopropyl iodide. From this isopropyl alcohol may be prepared (p. 115). The latter alcohol can also be derived by reduction from acetone, its oxidation product.

Secondary or Isopropyl Alcohol, *dimethyl carbinol*, was prepared in 1855 by Berthelot from propylene and sulphuric acid (p. 113), and in 1862 by Friedel, from acetone. Kolbe (Z. Ch., 1862, 687) recognized in isopropyl alcohol the first representative of the class of secondary alcohols predicted by him (p. 110).

It may be obtained from propylene oxide,  $\begin{matrix} CH_3 . CH \\ \dot{C}H_2 \end{matrix} > O$, by reduction, and from formic ester by the aid of zinc and methyl iodide. Its formation from normal propylamine by the action of nitrous acid is rather interesting. Primary propyl alcohol and propylene are produced at the same time.

The most practical method of obtaining it is to boil the iodide with ten parts of water and freshly prepared lead hydroxide in a vessel connected with a return condenser, or simply by heating the iodide with twenty volumes of water to 100° (A. 186, 391). Oxidation changes it to acetone, while chlorine converts it into tetrachloracetone (see this).

Trichlorisopropyl Alcohol,  $\begin{matrix} CCl_3 \\ CH_3 \end{matrix} > CH . OH$, is produced in the action of zinc methyl on chloral (p. 115). It is crystalline, fuses at 49°, and boils about 155° (A. 210, 78).

4. **Butyl Alcohols**, $C_4H_9 . OH$.—According to theory four isomerides are possible: 2 primary, 1 secondary, and 1 tertiary (p. 109):

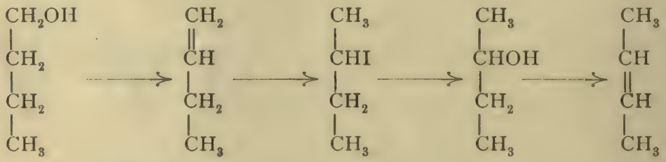
Name.	Formula.	M. P.	B. P.	Sp. Gr.
1. Normal Butyl Alcohol,	$CH_3(CH_2)_2CH_2OH$	Liquid	116.8°	0.8099 at 20°
2. Isobutyl Alcohol, . .	$(CH_3)_2.CH.CH_2OH$	"	108.4°	0.8020 at 20°
3. Secondary Butyl Alcohol, ...	$\begin{matrix}CH_3.CH_2\\ CH_3\end{matrix}\!>\!CH.OH$	"	99°	0.827 at 0°
4. Tertiary Butyl Alcohol,	$(CH_3)_3C.OH$	25°	83°	0.7788 at 30°

Normal Butyl Acohol, normal propyl carbinol [1-Butanol], forms in the action of sodium amalgam upon normal butyl aldehyde (Method, 4a, p. 113). It is further produced by a peculiar fermentation of glycerol, brought about in the presence of a schizomycetes (B. **16**, 1438; **29**, R. 72).

Trichlorbutyl Alcohol, $CH_3 . CHCl . CCl_2 . CH_2 . OH$, results when zinc ethyl and butyl chloral (p. 114) are brought together, and is also obtained from urobutylchloralic acid. It fuses at 62°, and boils under 45 mm. pressure at 120° (A. **213**, 372).

Methyl-ethyl Carbinol, *secondary butyl alcohol,* butylene hydrate, [2-Butanol], is a strongly-smelling liquid. It is obtained from normal butyl alcohol by its transposition into butylene,—with the splitting-off of water,—the addition of hydrogen iodide, and finally the saponification of the iodide (p. 115). The same iodide is formed on heating erythrite with hydriodic acid. Heated to 240°–250°, it decomposes into water and β-butylene, $CH_3 . CH : CH . CH_3$.

The genetic relations existing between the normal primary and secondary butyl alcohols, as well as between α-butylene and β-butylene, are shown in the following arrangement:



$$\begin{array}{c}CH_2OH\\ |\\ CH_2\\ |\\ CH_2\\ |\\ CH_3\end{array} \longrightarrow \begin{array}{c}CH_2\\ \|\\ CH\\ |\\ CH_2\\ |\\ CH_3\end{array} \longrightarrow \begin{array}{c}CH_3\\ |\\ CHI\\ |\\ CH_2\\ |\\ CH_3\end{array} \longrightarrow \begin{array}{c}CH_3\\ |\\ CHOH\\ |\\ CH_2\\ |\\ CH_3\end{array} \longrightarrow \begin{array}{c}CH_3\\ |\\ CH\\ \|\\ CH\\ |\\ CH_3\end{array}$$

Isobutyl Alcohol, *isopropyl carbinol, butyl alcohol of fermentation* [methyl 2-propanol-1], occurs in several fusel oils and especially in the spirit from potatoes. It is a liquid possessing a fusel-oil odor. It may be readily changed to isobutylene $(CH_3)_2C = CH_2$, from which, by the addition of halogen hydrides, derivatives of tertiary butyl alcohol are obtained (p. 94). For the action of chlorine upon isobutyl alcohol see B. **27**, R. 507; **29**, R. 992.

Trimethyl Carbinol, *tertiary butyl alcohol* [Dimethyl Ethanol], was prepared by Butlerow (1863) (A. **144**, 1) by the action of acetyl chloride upon zinc methyl (p. 114).

It was the first representative of the class of tertiary alcohols predicted by Kolbe.

The oxidation of tertiary butyl alcohol yields isobutyric acid $(CH_3)_2 . CH . CO_2H$ corresponding to isobutyl alcohol. This deportment may be explained by the intermediate formation of isobutylene $(CH_3)_2C = CH_2$, the conversion of the latter, by water absorption, into isobutyl alcohol and then oxidation of the latter (A. **189**, 73). The isobutylene, resulting from isobutyl alcohol and tertiary butyl alcohol, by the withdrawal of water can, by the addition of ClOH and reduction of the resulting chlorhydrin, be changed to isobutyl alcohol, and by absorption of HI yield tertiary butyl iodide, which in turn may be transformed into tertiary butyl alcohol (p. 115).

The boiling points of the haloid esters of the butyl alcohols will be given with the alkyl haloids (p. 140).

Amyl Alcohols, $C_5H_{11} . OH$.—Theoretically, 8 isomerides are possible: 4 primary alcohols, 3 secondary, and 1 tertiary. All are known.

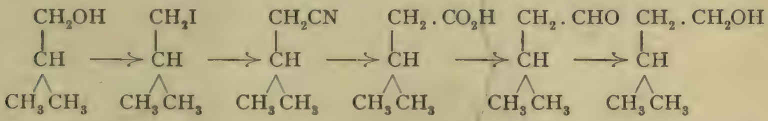
The following table contains the formulas and the boiling points of the eight amyl alcohols. The name amyl alcohol is derived from *ἄμυλον* = starch, because the first-discovered amyl alcohol was observed in the fusel oil formed from the brandy of potato starch.

Name.	Formula.	B. P.
1. Normal Amyl Alcohol, . .	$CH_3 . [CH_2]_3CH_2 . OH$	137°
2. **Isobutyl Carbinol,** . . .	$(CH_3)_2 . CHCH_2 . CH_2OH$	131.4°
3. **Active Amyl Alcohol,** . .	$\begin{matrix}CH_3\\ CH_3 . CH_2\end{matrix}>\overset{*}{C}H . CH_2OH$	128.7°
4. Tertiary Butyl Carbinol, . .	$(CH_3)_3C . CH_2OH$	102°
5. Diethyl Carbinol, ...	$(CH_3 . CH_2)_2CH . OH$	116°
6. Methyl n-propyl Carbinol, .	$\begin{matrix}CH_3\\ CH_3 . CH_2 . CH_2\end{matrix}>\overset{*}{C}H . OH$	118.5°
7. Methyl Isopropyl Carbinol, .	$\begin{matrix}CH_3\\ (CH_3)_2 . CH\end{matrix}>\overset{*}{C}H . OH$	112.5°
8. **Dimethyl Ethyl Carbinol,**	$\begin{matrix}(CH_3)_2\\ CH_3 . CH_2\end{matrix}>C . OH$	102.5°

Three of these eight alcohols contain an asymmetric carbon atom, indicated by a star, hence each can have three modifications, two optically active and one optically inactive modification (p. 46), which would raise the possible number of amyl alcohols to fourteen.

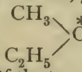
(1) **Normal Amyl Alcohol** is most easily prepared from normal amylamine (from caproic acid). It is almost insoluble in water, and has a fusel-oil odor.

(2) **Isobutyl Carbinol,** $(CH_3)_2CH . CH_2 . CH_2 . OH$, constitutes the chief ingredient of the amyl alcohol of fermentation obtained from fusel oil (p. 122), and occurs as esters of angelic and tiglic acids in Roman camomile oil. It may be obtained in a pure condition by synthesis from isobutyl alcohol, which it approaches in structure and with which it is associated in fusel oil:



The so-called alcohol of fermentation, possessing a disagreeable odor and boiling at 129–132°, occurs in fusel oil and consists mainly of inactive isobutyl carbinol. In addition, methyl-ethyl carbinol (active amyl alcohol) is present. It rotates the plane of polarization to the left; its activity is due to the presence of active amyl alcohol.

Fermentation amyl alcohol, treated with sulphuric acid, yields two amyl sulphuric acids. The different solubilities and crystalline forms of their barium salts distinguish them. From the more sparingly soluble salt, which forms in rather large quantity, isobutyl carbinol (Pasteur) may be obtained. A more complete separation of the alcohols is reached by conducting HCl into the mixture. Isobutyl carbinol will be etherified first, the active amyl alcohol remaining (Le Bel) (A. **220**, 149). The first upon oxidation yields inactive, and the second active valeric acid. When the crude fermentation alcohol is distilled with zinc chloride, ordinary amylene is the product. This consists mainly of $(CH_3)_2C:CH.CH_3$, resulting from a transposition of isobutyl carbinol; it contains, besides, γ-amylene and α-amylene (compare p. 94).

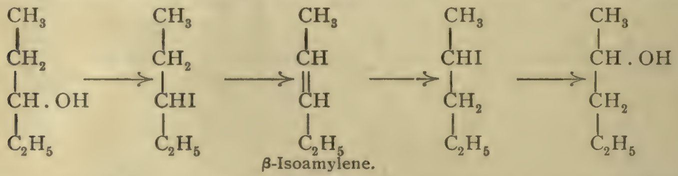


(3) **Active Amyl Alcohol,** $\begin{matrix}CH_3\\ C_2H_5\end{matrix}\!>\overset{*}{C}H\,.\,CH_2\,.\,OH$, *secondary butyl carbinol*, methyl-ethyl-carbin-carbinol. Of the two active modifications, the lævo-rotatory form, not yet obtained pure, is the optically active constituent of the fermentation alcohol. Its quantity in the fermentation alcohol equals about 13 per cent., and its rotatory power is $[\alpha]\,\delta = -5.2^\circ$. Its derivatives—*e. g.*, its chloride, bromide, iodide, and methyl-ethyl acetic acid (see valeric acid)—are all optically active and indeed dextro-rotatory (B. **28**, R. 410; **29**, 59).

Active amyl alcohol becomes inactive on boiling with NaOH (Le Bel). A mucor will render it again active, but dextro-rotatory (B. **15**, 1506).

(4) **Tertiary Butyl Carbinol,** $(CH_3)_3.C.CH_2.OH$, is formed on reducing the chloride of trimethyl-acetic acid or pivalic acid (B. **24**, R. 557) with sodium amalgam. It melts at 48–50°. Nitrous acid converts its amine, in consequence of a remarkable rearrangement of atoms, into dimethyl-ethyl carbinol (B. **24**, 2161).

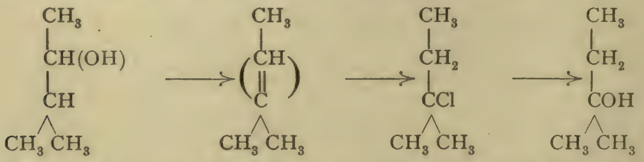
(5) **Diethyl Carbinol,** $(C_2H_5)_2.CH.OH$, is formed by the action of zinc and ethyl iodide upon ethyl formate. Since β-isoamylene, $C_2H_5.CH:CH.CH_3$, yields $C_2H_5.C_2H.CHI.CH_3$ with HI, from which methyl normal propyl carbinol is obtained, we can in this manner convert the diethyl carbinol into the latter alcohol:



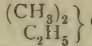
The two methyl propyl carbinols are obtained from methyl normal propyl ketone and methyl isopropyl ketone by reduction with sodium amalgam.

(6) **Methyl Normal Propyl Carbinol,** $CH_3.CH_2.CH_2.\overset{*}{C}H.OH.CH_3$, is made optically active (Le Bel) by *Penicillium glaucum*. The dextro-rotatory modification is destroyed, and the lævo-rotatory form remains.

(7) **Methyl Isopropyl Carbinol,** $(CH_3)_2.CH.CH(OH).CH_3$, yields, apparently, with the intermediate formation of amylene, when acted upon by halogen hydrides and also PCl_5, the derivatives of tertiary amyl alcohol:



The real derivatives of methyl isopropyl carbinol are obtained from α-isoamylene, $(CH_3)_2.CH.CH:CH_2$ (p. 94), by the addition of halogen hydrides at ordinary temperatures or when warmed.

(8) **Tertiary Amyl Alcohol,**  $\left.\begin{matrix}(CH_3)_2\\ C_2H_5\end{matrix}\right\}C.OH$, *dimethyl ethyl carbinol*, amylene hydrate, is a liquid with an odor like that of camphor. It produces sleep, the same as chloral hydrate, and is, therefore, made on a technical scale. Since ordinary amylene consists chiefly of β-isoamylene (p. 94), tertiary amyl alcohol is most practically prepared from the first by shaking it at —20° with sulphuric acid diluted with ½–1 volume of water and boiling the solution with water (A. **190**, 345).

It is further formed by the action of nitrous acid on the amine of tertiary butyl carbinol (B. **24**, 2519), and from propionyl chloride and zinc methide. At 200° it decomposes into water and β-isoamylene.

HIGHER HOMOLOGUES OF THE LIMIT-ALCOHOLS, $C_nH_{2n+1}.OH$.

There are many representatives of the higher homologues of the alcohols of this series. Fourteen of the seventeen theoretically possible hexyl alcohols and thirteen of the thirty-eight theoretically possible heptyl alcohols have been prepared. The higher we ascend in the series, the larger the number of theoretically possible members and the smaller the number of those alcohols which are actually known. Only a few of them are noteworthy either from a point of formation, structure, or occurrence in the animal or vegetable kingdoms. In the following arrangement will be found chiefly the names, formulas, melting points, and boiling points of normal alcohols:

Name.	Formula.	M. P.	B. P.
n-Hexyl Alcohol, ...	$CH_3.(CH_2)_4CH_2.OH$	. .	157°
Pinacolyl Alcohol, ...	$(CH_3)_3CCHOH.CH_3$	+4°	120°
n-Heptyl Alcohol, ...	$CH_3(CH_2)_5CH_2OH$	. .	175°
Pentamethyl-ethyl Alcohol, . .	$(CH_3)_3C.C(CH_3)_2OH$	+17°	131°
n-Octyl Alcohol, ...	$CH_3.(CH_2)_6.CH_2OH$	. .	199°
Cetyl Alcohol or Ethal, ...	$CH_3(CH_2)_{14}.CH_2OH$	+49.5°	340°
Ceryl Alcohol or Cerotin, . . .	$C_{27}H_{55}.OH$	79°	. .
Melissyl or Myricyl Alcohol, . .	$C_{30}H_{61}.OH$	85°	. .

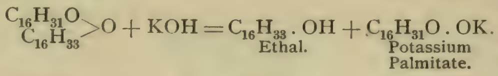
n-**Hexyl Alcohol** occurs as acetic and butyric esters in the oil of the seed of *Heracleum giganteum* (A. **163**, 193).

Pinacolyl Alcohol has a camphor-like odor. It results from the reduction of pinacoline (see this) or tertiary butyl methyl ketone, $(CH_3)_3.C.CO.CH_3$. See B. **26**, R. 14, for its transposition products.

n-*Heptyl Alcohol* has been prepared from oenanthol (see this) by reduction and from n-heptane (A. **161**, 278).

n-*Octyl Alcohol*, $C_8H_{17}OH$, occurs as acetic ester in the volatile oil of *Heracleum sphondylium*, as butyric ester in the oil of *Pastinaca sativa*, and in the oil of *Heracleum giganteum* (A. **185**, 26).

Cetyl Alcohol, $C_{16}H_{33}.OH$, **Hexadecyl Alcohol,** formerly called *ethal*, is a white, crystalline mass fusing at 49.5°, and distilling about 340°. It was prepared in 1818 by Chevreul from the cetyl ester of palmitic acid, the chief ingredient of spermaceti, by saponification with alcoholic potash:



$$\left.\begin{matrix}C_{16}H_{31}O\\C_{16}H_{33}\end{matrix}\right>O + KOH = \underset{\text{Ethal.}}{C_{16}H_{33}\,.\,OH} + \underset{\text{Potassium Palmitate.}}{C_{16}H_{31}O\,.\,OK}.$$

It yields, when fused with potassium hydroxide, palmitic acid (p. 117):

$$C_{15}H_{31}CH_2OH + KOH = C_{15}H_{31}COOK + 2H_2.$$

Ceryl Alcohol, $C_{27}H_{55}\,.\,OH$, *cerotin*, as ceryl cerotic ester, $C_{27}H_{53}O\,.\,O\,.\,C_{27}H_{55}$, constitutes Chinese wax. It is obtained by melting the latter with caustic potash. Ceryl alcohol is a white, crystalline mass, fusing at 79°. It yields cerotic acid when fused with potassium hydroxide.

Melissyl Alcohol, $C_{30}H_{61}\,.\,OH$, *myricyl alcohol*, occurs as myricyl palmitate in beeswax. It is isolated in the same manner as the preceding compound, and melts at 85°. Its *chloride* melts at 64°, and the *iodide* at 69.5°. Myricyl iodide and metallic sodium gave *Hexacontane*, $C_{60}H_{122}$, or dimyricyl (p. 84).

B. UNSATURATED ALCOHOLS.

1. OLEFINE ALCOHOLS, $C_nH_{2n-1}.OH$.

These are derived from the unsaturated alkylens, C_nH_{2n}, in the same manner as the normal alcohols are obtained from their hydrocarbons. In addition to the general character of alcohols, they are also capable of directly binding two additional affinities.

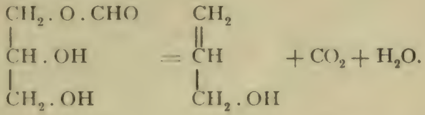
The chief representative of the class is allyl alcohol, $CH_2 = CH\,.\,CH_2OH$. When oxidized by potassium permanganate, the double linkage of the allyl alcohols is severed, and trihydric alcohols—glycerols—result (B. **21**, 3347).

1. **Vinyl Alcohol,** *vinol*, $CH_2:CH\,.\,OH$, separates as $C_2H_3O_2Hg_3Cl_2$ from ethyl ether on the addition to it of an alkaline mercury monoxychloride solution (Poleck and Thümmel, B. **22**, 2863). It is simultaneously produced with hydrogen peroxide when ether is oxidized with atmospheric oxygen. It cannot be separated from its mercury derivative because in all the reactions in which it should form, the isomeric acetaldehyde, $CH_3\,.\,CHO$, is produced (p. 53). It seems to be the universal rule that the atomic grouping $= C:CH\,.\,OH$, in the act of formation, is transposed into $= CH\,.\,CHO$ (Erlenmeyer, Sr., B. **13**, 309; **14**, 320); however, there are more stable bodies than vinyl alcohol, in which the groupings $= C = CH\,.\,OH$ and $= C = C(OH)R$ (p. **131**) are present.

The haloid esters of vinyl alcohol are to be considered the monohalogen substitution products of ethylene (p. **105**). Vinyl ether and vinyl ethyl ether are known (p. 136). The radical *vinyl* is present in neurine, so important physiologically.

2. **Allyl Alcohol** [*Propenol-3*], $C_3H_5\,.\,OH = CH_2:CH\,.\,CH_2\,.\,OH$.—Allyl compounds occur in the vegetable kingdom: allyl sulphide in oil of garlic, and allyl sulphocyanide, $C_3H_5N = C = S$, in oil of mustard. It may be prepared (1) by heating allyl iodide to 100° with 20 parts water; (2) it is produced, also, when nascent hydrogen acts upon acroleïn, $CH_2:CH\,.\,COH$, and (3) sodium upon dichlorhydrin, $CH_2Cl\,.\,CHCl\,.\,CH_2\,.\,OH$ (B. **24**, 2670). (4) It is best obtained from glycerol by heating the latter with formic or oxalic acid (A. **167**, 222).

In this reaction the oxalic acid at first breaks down into carbon dioxide and formic acid, which forms an ester with the glycerol; this then decomposes into allyl alcohol, carbon dioxide, and water:



$$\begin{array}{l} CH_2 . O . CHO \\ | \\ CH . OH \\ | \\ CH_2 . OH \end{array} = \begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CH_2 . OH \end{array} + CO_2 + H_2O.$$

Allyl alcohol is a mobile liquid with a pungent odor, boiling at 96–97°, and having at 20° a specific gravity of 0.8540. It solidifies at —50°. It is miscible with water, and burns with a bright flame.

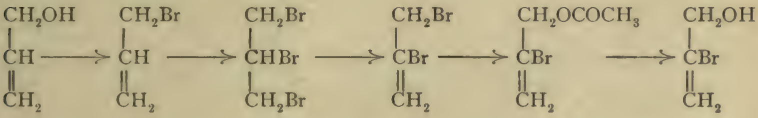
It yields acroleïn and acrylic acid when oxidized with silver oxide, and only *formic acid* (no acetic) when chromic acid is the oxidizing agent. *Glycerol* results when potassium permanganate is the oxidant. Nascent hydrogen is apparently without effect upon it, as seems to be indicated by its formation from acroleïn. Chlorine partly oxidizes it, and again adds itself, giving rise to acroleïn and the dichlorhydrin of glycerol (B. **24**, 2670). When heated to 150° with caustic potash, formic acid, normal propyl alcohol, and other products are obtained.

Allyl alcohol, heated with mineral acids, yields propionic aldehyde and methyl ethyl acroleïn (B. **20**, R. 699).

Halogen Allyl Alcohols have been obtained from α- and β-dichlorpropylene and β-dibrompropylene.

α-Chlorallyl Alcohol, $CH_2 = CCl . CH_2OH$, boils at 136°.
β-Chlorallyl Alcohol, $CHCl = CH . CH_2OH$, boils at 153°.
α-Bromallyl Alcohol, $CH_2 = CBr . CH_2OH$, boils at 152°.

Sulphuric acid, acting upon α-chlorallyl alcohol, produces acetone-alcohol (see this), and with α-bromallyl alcohol yielded propargyl alcohol (see p. 132). α-Bromallyl alcohol may be prepared from allyl alcohol by a series of reactions, shown in the following diagram:



$$\begin{array}{l} CH_2OH \\ | \\ CH \\ \| \\ CH_2 \end{array} \longrightarrow \begin{array}{l} CH_2Br \\ | \\ CH \\ \| \\ CH_2 \end{array} \longrightarrow \begin{array}{l} CH_2Br \\ | \\ CHBr \\ | \\ CH_2Br \end{array} \longrightarrow \begin{array}{l} CH_2Br \\ | \\ CBr \\ \| \\ CH_2 \end{array} \longrightarrow \begin{array}{l} CH_2OCOCH_3 \\ | \\ CBr \\ \| \\ CH_2 \end{array} \longrightarrow \begin{array}{l} CH_2OH \\ | \\ CBr \\ \| \\ CH_2 \end{array}$$

(3) *β-Allyl Alcohol*, $CH_2 = C(OH) . CH_3$, is only known in its ether (p. 136). *Sodium-β-allyl alcoholate* is produced by the action of metallic sodium upon acetone (A. **278**, 116), diluted with anhydrous ether.

(4) **Crotonyl Alcohol**, $C_4H_7 . OH = CH_3 . CH : CH . CH_2 . OH$, is obtained from crotonaldehyde, $CH_3 . CH : CH . CHO$, by means of nascent hydrogen. It boils at 117–120°.

Higher Unsaturated Alcohols of the allyl series, having secondary and tertiary structure, arise in the action of zinc and allyl iodide upon aldehydes (B. **27**, 2434) and ketones, p. 114 (B. **17**, R. 316; A. **185**, 151, 175; **196**, 109; Jr. pr. Ch. [2], **30**, 399), as well as by action of zinc alkyls upon unsaturated aldehydes.

Dimethyl Allyl Carbinol, $CH_2 = CH . CH_2C(CH_3)_2OH$, boils at 119.5°. *Diethyl allyl carbinol* boils at 156°. *Methyl propyl allyl carbinol* boils at 159–160°.

UNSATURATED ALCOHOLS, $C_nH_{2n-3} . OH$.

To this class belong:

Alcohols containing a pair of trebly linked carbon atoms, and *alcohols* which contain two pairs of doubly linked carbon atoms. Propargyl alcohol is the only well-known member of the *acetylene series*, whereas various alcohols, derived from *diolefines*, have not only been synthetically prepared, but have also been discovered in ethereal oils.

2. ACETYLENE ALCOHOLS.

Propargyl Alcohol [*Propinol*-3], $C_3H_4O = CH : C . CH_2OH$.—This alcohol was obtained by Henry in 1872 (B. 5, 569; 8, 389) upon treating α-bromallyl alcohol (see p. 131) with caustic potash.

Propargyl alcohol is a mobile, agreeable-smelling liquid, with a specific gravity at 20° of 0.9715. It boils at 114–115°.

Like acetylene, it forms an explosive silver compound, $C_3H_2(OH)Ag$, white in color. The copper salt, $(C_3H_2OH)_2Cu$, is a yellow precipitate.

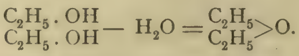
3. DIOLEFINE ALCOHOLS.

Higher alcohols, in which the double union of carbon atoms occurs twice, are synthetically produced by the action of zinc and allyl iodide upon ethers of formic acid and even of acetic acid (A. 197, 70). Diolefine alcohols, which can be transposed into terpenes, are of great theoretical interest. Such are geraniol or rhodinol and linalool. They will be discussed under the terpenogen group.

ALCOHOL DERIVATIVES.

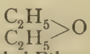
1. SIMPLE AND MIXED ETHERS.

Ethers are the oxides of the alcohol radicals. If the alcohols are compared with basic hydrates, then the ethers are analogous to the metallic oxides. They may be considered also as anhydrides of the alcohols, formed by the elimination of water from two molecules of alcohol:



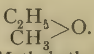
$$\begin{matrix} C_2H_5 . OH \\ C_2H_5 . OH \end{matrix} - H_2O = \begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}\!>O.$$

Ethers containing two similar alcohol radicals are termed *simple ethers*; those with different radicals, *mixed ethers*:



$$\begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}\!>O$$

Ethyl Ether, or
Diethyl Ether.

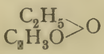


$$\begin{matrix} C_2H_5 \\ CH_3 \end{matrix}\!>O.$$

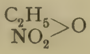
Methyl-ethyl
Ether.

The metamerism of ethers among themselves is dependent upon the homology of the alcohol radicals, held together by oxygen (p. 41).

We must make a distinction between the above and the so-called compound ethers or *esters*, in which both an alcohol radical and an acid radical are present—*e. g.*:



$$\begin{matrix} C_2H_5 \\ C_2H_3O \end{matrix}\!>O$$ Ethyl Acetic Ester; and

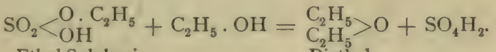


$$\begin{matrix} C_2H_5 \\ NO_2 \end{matrix}\!>O$$ Ethyl Nitric Ester.

The properties of these are entirely different from those of the alcohol ethers. In the following pages they will always be termed *esters*.

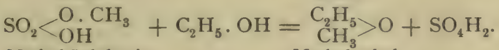
The following are the most important methods of preparing ethers:

1. Their most important method of formation consists of the interaction of *sulphuric acid* and *alcohols*. Alkyl sulphuric acids result at first, but on further heating with alcohols these are rearranged into ethers. This procedure affords a means of obtaining both simple and mixed ethers (Williamson, Chancel):



$$SO_2{<}\begin{matrix}O\,.\,C_2H_5\\OH\end{matrix} + C_2H_5\,.\,OH = \begin{matrix}C_2H_5\\C_2H_5\end{matrix}{>}O + SO_4H_2.$$

Ethyl Sulphuric Acid. Diethyl Ether.



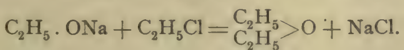
$$SO_2{<}\begin{matrix}O\,.\,CH_3\\OH\end{matrix} + C_2H_5\,.\,OH = \begin{matrix}C_2H_5\\CH_3\end{matrix}{>}O + SO_4H_2.$$

Methyl Sulphuric Acid. Methyl-ethyl Ether.

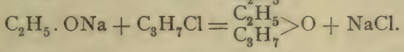
When a mixture of two alcohols is permitted to act upon sulphuric acid, three ethers are simultaneously formed; two are simple and one is a mixed ether. Other polybasic acids, like phosphoric, arsenic, and boric, behave like sulphuric acid. This is also true of hydrochloric acid at 170°, and sulpho-acids—*e. g.*, benzene sulphonic acid, at 145° (F. Krafft, B. **26**, 2829). In this reaction ethyl benzene sulphonic ester is produced and breaks down in the sense of the equations:

$$C_6H_5SO_3H + C_2H_5OH = C_6H_5SO_3C_2H_5 + H_2O.$$
$$C_6H_5SO_3C_2H_5 + C_2H_5OH = C_6H_5SO_3H + (C_2H_5)_2O.$$

2. The action of the alkylogens upon the sodium alcoholates in alcoholic solution. Mixed ethers are also formed here:



$$C_2H_5\,.\,ONa + C_2H_5Cl = \begin{matrix}C_2H_5\\C_2H_5\end{matrix}{>}O + NaCl.$$



$$C_2H_5\,.\,ONa + C_3H_7Cl = \begin{matrix}C_2H_5\\C_3H_7\end{matrix}{>}O + NaCl.$$

Consult B. **22**, R. 381, 637, upon the speed of these reactions.

3. Action of the alkylogens upon metallic oxides, especially silver oxide:

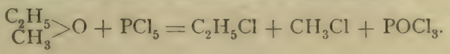
$$2C_2H_5I + Ag_2O = (C_2H_5)_2O + 2AgI.$$

The constitution of ethers is indicated in this reaction.

Properties.—Ethers are neutral, volatile (hence the name αἰθήρ, air) bodies, nearly insoluble in water. The lowest members are gases; the next higher are liquids, and the highest—*e. g.*, cetyl ether—are solids. Their boiling points are very much lower than those of the corresponding alcohols (A. **243**, 1).

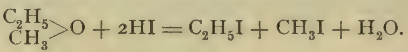
Transpositions.—Chemically, ethers are very indifferent, because all the hydrogen is attached to carbon.

(1) When oxidized they yield the same products as their alcohols.
(2) They yield ethereal salts when heated with concentrated sulphuric acid.
(3) Phosphorus chloride converts them into alkyl chlorides:



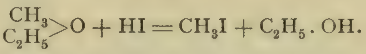
$$\begin{matrix}C_2H_5\\CH_3\end{matrix}{>}O + PCl_5 = C_2H_5Cl + CH_3Cl + POCl_3.$$

(4) The same occurs when they are heated with the haloid acids, especially with HI:



$$\begin{matrix}C_2H_5\\CH_3\end{matrix}{>}O + 2HI = C_2H_5I + CH_3I + H_2O.$$

When acted upon by HI in the cold, they decompose into alcohol and an iodide. With mixed ethers it is the iodide of the lower radical that is invariably produced (B. **9**, 852; **26**, R. 718).



$$\begin{matrix}CH_3\\C_2H_5\end{matrix}{>}O + HI = CH_3I + C_2H_5 . OH.$$

(5) Many ethers, especially those with secondary and tertiary alkyls and those with unsaturated alkyls (allyl), break up into alcohols (B. **10**, 1903) when heated with water or dilute sulphuric acid to 150°.

A. ETHERS OF THE SATURATED OR PARAFFIN ALCOHOLS.

Methyl Ether, $(CH_3)_2O$, is prepared by heating methyl alcohol with sulphuric acid (B. **7**, 699). It is an agreeable-smelling gas, which may be condensed to a liquid at about —23°. Water dissolves 37 volumes and sulphuric acid upward of 600 volumes of the gas.

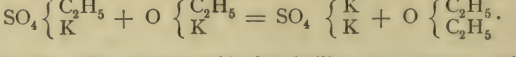
Chlorine converts ether into chlormethyl ether, s-dichlormethyl ether, and perchlormethyl ether, which decomposes on boiling. The first two are formaldehyde derivatives, and, together with the corresponding brom- and iodo-compounds, will be treated after formaldehyde.

Ethyl Ether or **Ether,** $(C_2H_5)_2O$, is by far the most important representative of this class of compounds. It has been known for a long time.

History.—Ethyl ether and its production from alcohol and sulphuric acid were known in the sixteenth century. They were described by *Valerius Cordus*, a German physician. Until the beginning of the present century ether was regarded as a sulphur-containing body; hence, to distinguish it from other ethereal compounds, it was called *sulphur-ether*. The ether process, in which a comparatively small quantity of sulphuric acid was capable of converting a large quantity of alcohol into ether, was included in the category of *catalytic reactions*. The explanation of this process constitutes one of the most brilliant advances in organic chemistry.

In 1842, Gerhardt, from purely theoretical reasons and in opposition to Liebig, concluded that the ether molecule did not contain the same number of carbon atoms as were present in the alcohol molecule, but exactly *twice* that number. He was unable to gain general acceptance for this view. Williamson, in 1850, by a new synthesis of ether, proved the correctness of Gerhardt's conception, not only for it, but for ethers in general. His method was the transposition taking place between sodium ethylate and ethyl iodide (p. 133). The formation of ether from alcohol and sulphuric acid Williamson explained by a continuous breaking-down and re-formation of ethyl sulphuric acid, made possible by the contact of alcohol with the acid at 140° (A **77**, 37; **81**, 73).

Chancel, who preceded Williamson in publication, had made ether independently of the latter, by heating a mixture of potassium ethyl sulphate and potassium ethylate:



$$SO_4\left\{\begin{matrix}C_2H_5\\K\end{matrix}\right. + O\left\{\begin{matrix}C_2H_5\\K\end{matrix}\right. = SO_4\left\{\begin{matrix}K\\K\end{matrix}\right. + O\left\{\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right..$$

The objection that ether, because of its low boiling temperature, could not contain the double number of carbon atoms in its molecule, Chancel removed by citing the boiling point of ethyl acetic ester (Compt. rend. par Laurent et Gerhardt (1850), **6**, 369).

Ethyl Alcohol,	C_2H_5OH,	boils at 78°.
Ether,	$(C_2H_5)_2O$,	boils at 35°.
Acetic Acid,	CH_3CO_2H,	boils at 118°.
Ethyl Acetic Ester,	$CH_3 . CO_2 . C_2H_5$,	boils at 77°.

Thus was proved that ethyl alcohol and ether were bodies belonging to the *water type* (p. 35)—*i. e.*, they might be regarded as water in which one and two hydrogen atoms were replaced by ethyl:

$$\left.\begin{matrix}H\\H\end{matrix}\right\}O \qquad \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O \qquad \left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O.$$

Preparation.—Ether is made (1) from ethyl alcohol and sulphuric acid heated to 140°. The process is continuous. (2) From benzene sulphonic acid and alcohol at 135–145° (B. **26**, 2829).

The advantage in the second method is that the ether is not contaminated with sulphur dioxide, which in the first method is removed from the crude product by washing with a soda solution. Anhydrous ether may be obtained by distilling ordinary ether over burnt lime, and drying it finally with sodium wire (see aceto-acetic ester) until there is no further evolution of hydrogen.

Test for Water and Alcohol.—When ether containing water is shaken with an equal volume of CS_2, a turbidity results. When alcohol is present, the ether, on shaking with aniline violet, is colored. Anhydrous ether does not acquire a color when similarly treated.

Properties.—Ethyl ether is a mobile liquid with peculiar odor, and specific gravity at 0° of 0.736. When anhydrous, it does not congeal at —80°. It boils at 35° and evaporates very rapidly even at medium temperatures. It dissolves in 10 parts of water and is miscible with alcohol. Nearly all the carbon compounds insoluble in water, such as the fats and resins, are soluble in ether. It is extremely inflammable, burning with a luminous flame. Its vapor forms a very explosive mixture with air. When inhaled, ether vapor brings about unconsciousness, a property discovered in 1842 by Charles Jackson, of Boston, hence its use in surgical operations.* *Hoffmann's Anodyne* (so named after the great Halle clinician, who died in 1742) is a mixture of 3 parts alcohol and 1 part ether.

Ether unites with bromine to form peculiar, crystalline addition products, somewhat like bromine hydrate; it combines, too, with water and metallic salts.

Transpositions.—For the action of air on ether see vinyl alcohol (p. 130). Hydrogen peroxide is produced when oxygen acts on moist ether (B. **29**, R. 840). When heated with water and sulphuric acid to 180°, ethyl alcohol results. When ozone is conducted into anhydrous ether, an explosive peroxide is formed.

Chlorine, acting upon cooled ether, produces (A. **279**, 301):

Monochlor-ether,	$CH_3 . CHCl . O . C_2H_5$,	boiling at 98°.
1. 2-*Dichlor-ether*,	$CH_2Cl . CHCl . O . C_2H_5$,	boiling at 145°.
Trichlor-ether,	$CHCl_2 . CHCl . O . C_2H_5$,	boiling at 102° (100 mm.).
Perchlor-ether,	$(C_2Cl_5)_2O$,	melting at 68°. It breaks down

on distillation into C_2Cl_6 and trichlor-acetyl chloride, $C_2Cl_3O . Cl$.

2-Cl-, Br-, I-*ethyl ethers* are the ethers of glycol-, chlor-, brom-, and iodhydrins—*e. g.*, $CH_2Cl . CH_2 . O . C_2H_5$.

---

* Der Aether gegen den Schmerz, von Binz in Bonn, 1896.

s-*Dichlor-ether*, $CH_3 . CHCl . O . CHCl . CH_3$, boiling at 116°, is produced by the action of hydrochloric acid upon aldehyde.

The following table contains the melting and boiling points of the better known simple and mixed ethers:

Ethyl methyl ether boils at 11°; n-*propyl-methyl ether* boils at 50°; n-*propyl ether* boils at 86°; *isopropyl ether* boils at 60–62°; *isoamyl ether* boils at 176°; *Cetyl ether*, $(C_{16}H_{33})_2O$, melts at 55° and boils at 300°.

B. ETHERS OF UNSATURATED ALCOHOLS.

It was explained, when discussing the unsaturated alcohols (p. 130), that the members of that series in which hydroxyl was combined with a doubly linked carbon atom readily rearranged themselves into aldehydes or ketones, and were only known in their derivatives, especially as *ethers*. Thus:

1. *Vinyl ether*, $(CH_2 = CH)_2O$, boils at 39°, and may be obtained from vinyl sulphide (p. 149) and silver oxide. 2. *Perchlor-vinyl ether*, *Chloroxethose*, $(CCl_2 = CCl)_2O$, is formed from perchlorethyl ether (p. 135) and K_2S. 3. *Vinyl ethyl ether*, boiling at 35.5°, results from the interaction of iodoethyl ether and sodium ethylate. 4. *Isopropenyl-ethyl ether*, $CH_3C(OC_2H_5) = CH_2$, formed from propenyl bromide and alcoholic potash, or from ethoxycrotonic acid (B. 29, 1005), boils at 62–63°.

Ethers of allyl alcohol and propargyl alcohol are known: *Allyl ether*, $(CH_2 = CH . CH_2)_2O$, boils at 85°; *propargyl ethyl ether*, $CH \equiv C . CH_2 . O . CH_2 . CH_3$, boils at 80°. See ethyl propiolic ester.

2. ESTERS OF THE MINERAL ACIDS.

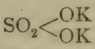
If we compare the alcohols with the metallic bases, the esters or compound ethers (p. 132) are perfectly analogous in constitution to the salts. Just as salts result from the union of metallic hydroxides with acids, so esters are formed by the combination of alcohols with acids. Water appears as a side-product in both reactions:

$$NaOH + HCl = NaCl + H_2O.$$
$$C_2H_5OH + HCl = C_2H_5Cl + H_2O.$$

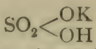
The haloid esters correspond to the haloid salts; they may also be regarded as monohalogen substitution products of the hydrocarbons (p. 101). Corresponding to the oxygen salts are the esters of other acids, which, therefore, may be viewed as derivatives of the alcohols, in which the *alcohol-hydrogen* has been replaced by acid radicals, or as derivatives of the acids, in which the hydrogen replaceable by metals has been substituted by alcohol radicals. The haloid esters would be included in the last definition of esters. The various definitions of esters as derivatives of the acids, and again as derivatives of the alcohols, find expression in the different designations of the esters:

$$\underset{\text{Ethyl Nitrate.}}{C_2H_5 . O . NO_2} \quad \text{or} \quad \underset{\text{Nitric Ethyl Ester.}}{NO_2 . O . C_2H_5.}$$

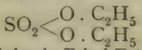
In polybasic acids all the hydrogen atoms can be replaced by alcohol radicals resulting in the production of *neutral esters*. When alcohol radicals are introduced for all of the hydrogen atoms *acid esters* are formed. These still possess the acid character. They form salts, hence are termed *ether acids*, and correspond to acid salts:


$SO_2<\begin{matrix}OK\\OK\end{matrix}$

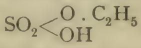
Neutral Potassium Sulphate.


$SO_2<\begin{matrix}OK\\OH\end{matrix}$

Acid Potassium Sulphate.


$SO_2<\begin{matrix}O\,.\,C_2H_5\\O\,.\,C_2H_5\end{matrix}$

Sulphuric Ethyl Ester.


$SO_2<\begin{matrix}O\,.\,C_2H_5\\OH\end{matrix}$

Ethyl Sulphuric Acid.

Dibasic acids form two series of salts, and also of esters, while with tribasic acids there are three series of salts and of esters.

In the case of the polyhydric alcohols there are, besides the neutral esters, also *basic esters*, corresponding to the basic salts, in which not all of the hydroxyl groups participated in the esterification.

Formation of Esters.—(1) The esters can be prepared by allowing alcohols and acids to act directly; water is also produced:

$$C_2H_5\,.\,OH + NO_2\,.\,OH = C_2H_5\,.\,O\,.\,NO_2 + H_2O.$$

This transposition, however, only takes place gradually, progressing with time; it is accelerated by heat, but is never complete. We always find alcohols and acids together with the esters, and they do not react any further upon each other. If the *ester* be removed—*e. g.*, by distillation—from the mixture, as it is formed, an almost perfect reaction may be attained.

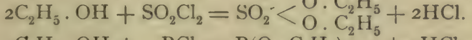
When acted upon by alcohols, the polybasic acids mostly yield the primary esters or ether-acids.

There are two synthetic methods of producing the esters which favor the views of considering them derivatives of alcohols or acids. These are:

(2) By reacting on the acids (their silver or alkali salts) with alkylogens:

$$NO_2\,.\,O\,.\,Ag + C_2H_5I = NO_2\,.\,O\,.\,C_2H_5 + AgI.$$

(3) By acting upon the alcohols or metallic alcoholates with acid chlorides:


$$2C_2H_5\,.\,OH + SO_2Cl_2 = SO_2<\begin{matrix}O\,.\,C_2H_5\\O\,.\,C_2H_5\end{matrix} + 2HCl.$$

$$3C_2H_5\,.\,OH + BCl_3 = B(O\,.\,C_2H_5)_3 + 3HCl.$$

Properties.—The neutral esters are insoluble, or soluble with difficulty in water, and almost all are volatile; therefore the determination of their vapor density is a convenient means of establishing the molecular magnitude and also the basicity of the acids. The ether-acids are not volatile, but are soluble in water and yield salts with the bases.

All esters, and especially the ether-acids, are decomposed into alcohols and acids (p. 112) when heated with water. Sodium and potassium hydroxides, in aqueous or alkaline solution, accomplish this with great readiness when aided by heat. The process is termed *saponification*, because the *soaps—i. e.*, the potassium and sodium salts of the higher fatty acids (see these)—are obtained by this reaction from the fats, the glycerol esters:

$$NO_2\,.\,O\,.\,C_2H_5 + KOH = C_2H_5OH + NO_2OK.$$

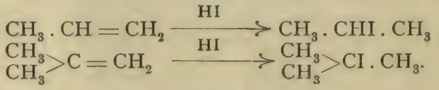
A. I. ALKYL ESTERS OF THE HALOID ACIDS, HALOID ESTERS OF THE SATURATED ALCOHOLS, ALKYLOGENS.

It was pointed out under the halogen substitution products of the paraffins and the unsaturated acyclic hydrocarbons that the *monohalogen* substitution products, or *alkylogens*, were largely prepared from the alcohols as starting-out substances. This intimate connection with the alcohols is the reason for the assumption of the alkylogens as esters of the haloid acids. As haloid esters of the alcohols they arrange themselves with the alkyl esters of the inorganic oxygen acids.

The view that the halogen derivatives $C_nH_{2n+1}X$ are paraffin substitution products is expressed in the names monochlor-methane, monochlor-ethane, etc., while the designation methyl chloride, ethyl chloride, etc., preferred for the monohalogen substitution derivatives of methane and ethane, mark these substances as haloid esters of the alcohols, corresponding to the metallic halides.

Formation of Alkylogens.—(1) *By the substitution of the paraffins.* The conditions favoring the substitution of the hydrogen atoms of the paraffins by halogen atoms have been mentioned under the general methods for the preparation of halogen substitution products. The substitution reaction is not well adapted for the preparation of alkylogens, because mixtures of compounds are invariably produced. In the higher members of the series isomerides are formed. This is because the chlorine enters for the hydrogen both of terminal and intermediate carbon atoms. Thus normal pentane, $CH_3.CH_2.CH_2.CH_2.CH_3$, yields $CH_3.CH_2.CH_2.CH_2.CH_2Cl$ and $CH_3.CH_2.CH_2.CHCl.CH_3$, and such mixtures are separated with great difficulty.

(2) *By the addition of haloid acids to the olefines.* In this addition, which occurs with especial ease with hydrogen iodide, it is interesting to note that the halogen atom attaches itself to the carbon atom carrying the least amount of hydrogen (p. 93):



$$CH_3.CH=CH_2 \xrightarrow{HI} CH_3.CHI.CH_3$$
$$\begin{matrix}CH_3\\CH_3\end{matrix}{>}C=CH_2 \xrightarrow{HI} \begin{matrix}CH_3\\CH_3\end{matrix}{>}CI.CH_3.$$

(3) *From alcohols* (a) *by the action of haloid acids.* This reaction does not readily complete itself unless the halogen hydride is used in great excess, or the water formed at the same time with the alkylogen is absorbed. Hence in the case of methyl and ethyl alcohol an addition of zinc chloride or sulphuric acid is advantageous (see mono-chlor-methane, p. 141).

This addition is a disadvantage with the higher alcohols, because then olefines are first produced, and to these the halogen hydride adds itself in such a manner that an isomeride of the desired alkylogen is obtained (p. 92). It may also be remarked that in the presence of an excess of hydriodic acid the iodides are often reduced. Hence alkyl iodides can be prepared from polyhydric alcohols (compare isopropyl iodide, p. 142):

$$C_2H_4(OH)_2 + 3HI = C_2H_5I + I_2 + 2H_2O.$$
$$C_3H_5(OH)_3 + 5HI = C_3H_7 + 2I_2 + 3H_2O.$$
$$C_4H_6(OH)_4 + 7HI = C_4H_9I + 3I_2 + 4H_2O.$$
$$C_6H_8(OH)_6 + 11HI = C_6H_{13}I + 5I_2 + 6H_2O.$$

(b) *By the action of phosphorus halides.* If, for example, ethyl alcohol be treated with PCl_3, PBr_3, or PI_3, two possibilities arise: either an halogen hydride and ethyl phosphorous ether are produced, or an ethyl haloid and phosphorous acid. The latter reaction occurs when PBr_3 and PI_3 are used, and this method is adopted almost exclusively in the preparation of the alkyl bromides and iodides (see ethyl bromide and ethyl iodide):

$$PBr_3 + 3C_2H_5OH = 3C_2H_5Br + PO_3H_3$$
$$PI_3 + 3C_2H_5OH = 3C_2H_5I + PO_3H_3.$$

(BI_3 acts analogously upon ethyl alcohol, B. **24**, R. 387). The formation of esters of phosphorous acid by the use of PBr_3 and PI_3 is far from satisfactory. PCl_3, on the other hand, yields phosphorous esters and hydrochloric acid almost entirely according to the equation:

$$PCl_3 + 3C_2H_5OH = P(O.C_2H_5)_3 + 3HCl.$$

The chlorides are readily formed if PCl_5 be substituted for PCl_3:

$$PCl_5 + C_2H_5OH = C_2H_5Cl + HCl + POCl_3.$$

(4) *From alkyl-haloids or alkyl sulphuric acids and metallic halides.*

(a) Bromides and iodides can be transformed into chlorides by heating them with $HgCl_2$:

$$2C_3H_7I + HgCl_2 = 2C_3H_7Cl + HgI_2.$$

(b) When chlorides are heated with $AlBr_3$ or AlI_3 or CaI_2 they become bromides or iodides (B. **14**, 1709; **16**, 392; **19**, R. 166):

$$3C_2H_5Cl + AlBr_3 = 3C_2H_5Br + AlCl_3.$$

(c) Methyl and ethyl iodides yield with AgFl the gaseous compounds *methyl fluoride*, CH_3Fl, and *ethyl fluoride*, C_2H_5Fl, which have an agreeable, ethereal odor, and do not attack glass (B. **22**, R. 267).

(d) On distilling ethyl sulphuric acid and potassium bromide, ethyl bromide is produced.

Isomerism.—Propane is the first hydrocarbon yielding isomerides (p. 43). The isomerism depends on the varying position of the hydrogen atoms in the same carbon chain, and from butane forward it depends on the different linkage of the carbon atoms forming the carbon skeleton (see table, p. 140).

Properties and Transpositions.—The alkylogens are ethereal, agreeable, sweet-smelling liquids. They are scarcely soluble in water, but dissolve with ease in alcohol and ether. They are gases at the ordinary temperature—*e. g.*, methyl chloride, ethyl chloride, and methyl bromide. The chlorides boil 28°–20° lower than the bromides, and the latter from 34°–28° lower than the corresponding iodides (p. 140). The differences grow less with increasing molecular weight. As in the case of the hydrocarbons, so here it may be said that where isomerides exist, the normal members have the highest boiling points. The more branched the carbon chain, the lower will the boiling point lie.

As *haloid esters* of the alcohols, the alkylogens may be compared with the metallic halides, although the halogens are less readily transposed by silver nitrate. The iodides are the most reactive. However, the alkylogens are excellently adapted to bring about the replacement of metals, and thus unite atoms previously in union with metals, to alcohol radicals. Particularly interesting is the transposition occasioned by the alkaline cyanides (see nitriles), and the sodium derivatives of aceto-acetic ester (see this) and malonic ester (see this). Both are *synthetic reactions* of the first importance (p. 81). The alkylogens play a prominent part in the *nucleus-syntheses* of the paraffins (see ethane, p. 82). They constitute the transition from the paraffins and olefines to the alcohols (see these), into which they are converted by moist silver oxide.

The methods for the transposition of alcohols into ethers, into mercaptans, into alkyl sulphides (sulphur ethers) and compound mineral ethers or esters, are based upon the reactivity of the halogen atoms in the alkylogens. This is also the case with the methods employed in the preparation of metal alkyls.

Among the numerous reactions of the alkylogens, mention may here be made of their power to unite with ammonia and ammonium bases. By this means the primary, secondary, and tertiary amines, as well as the tetra alkyl ammonium halides, were obtained.

The following table contains the boiling points of some of the alkylogens at the ordinary pressure:

Name and Formula of Radical.		Chloride.	Bromide.	Iodide.
Methyl-,	$CH_3—$	—24°	+4.5°	43°
Ethyl-,	$CH_3 . CH_2—$	+12.5°	38°	72°
Norm. Propyl-,	$CH_3 . CH_2 . CH_2—$	44°	71°	102°
Isopropyl-,	$(CH_3)_2CH—$	36.5°	59.5°	89.5°
Norm. Butyl-,	$CH_3 . CH_2 . CH_2 . CH_2—$	77.5°	100.4°	129.6°
Isobutyl-,	$(CH_3)_2 . CH . CH_2—$	68.5°	92°	120°
Sec. Butyl-,	$\begin{matrix}CH_3\\C_2H_5\end{matrix}>CH—$	. . .	. . .	120°
Tert. Butyl-,	$(CH_3)_3C—$	51.5°	72°	103.3°
Norm. Amyl-,	$CH_3 . (CH_2)_3CH_2—$	106°	129°	155°
Isoamyl-	$(CH_3)_2CH . CH_2 . CH_2—$	100°	120°	148°
Diethyl Methyl-,	$(C_2H_5)_2CH—$	. . .	. . .	145°
Methyl-norm.-propyl Methyl-,	$\begin{matrix}CH_3\\CH_3 . CH_2 . CH_2\end{matrix}>CH—$	104°	113°	144°
Methyl-isopropyl-methyl-,	$\begin{matrix}CH_3\\(CH_3)_2CH\end{matrix}>CH—$	91°	115°	138°
Dimethyl-ethyl-methyl-,	$\begin{matrix}(CH_3)_2\\C_2H_5\end{matrix}>C—$	86°	100°	127°
Norm. Hexyl-,	$CH_3 . [CH_2]_4 . CH_2—$	133°	155°	179°
Norm. Heptyl-,	$CH_3 . [CH_2]_5 . CH_2—$	159°	178°	203°
Norm. Octyl-,	$CH_3 . [CH_2]_6 . CH_2—$	180°	199°	225°

Monochlormethane, CH_3Cl, **Methyl Chloride,** is obtained from methane or methyl alcohol. It is a sweet-smelling gas. Alcohol will dissolve 35 volumes of it, and water 4 volumes.

It is prepared by heating a mixture of 1 part methyl alcohol (wood spirit), 2 parts sodium chloride, and 3 parts sulphuric acid. A better plan is to conduct HCl into boiling methyl alcohol in the presence of zinc chloride (½ part). The disengaged gas is washed with KOH, and dried by means of sulphuric acid. Commercial methyl chloride usually occurs in a compressed condition. It was formerly applied in the manufacture of the aniline dyes, and in producing cold. It is obtained by heating trimethylamine hydrochloride, $N(CH_3)_3 . HCl$.

Monochlorethane, C_2H_5Cl, **Ethyl Chloride,** is an ethereal liquid, boiling at 12.5°; specific gravity at $0° = 0.921$. It is miscible with alcohol, but is sparingly soluble in water.

It is prepared from ethyl alcohol in the same manner that methyl chloride is obtained from its alcohol. Its formation from ethyl hydride or dimethyl by means of chlorine (p. 83) is important from a theoretical standpoint.

If heated with water to 100° (in a sealed tube), it changes to ethyl alcohol. The conversion is more rapid with potassium hydroxide. In dispersed sunlight, chlorine acts upon it to form ethylidene chloride, $CH_3 . CHCl_2$, and other substitution products. Of these C_2HCl_5 was formerly employed as *Æther anæstheticus.* Chlorine converts ethyl chloride, in the presence of iron, into ethylene chloride.

The boiling points of the two *propyl chlorides*, the three *butyl chlorides*, six *amyl chlorides*, normal *hexyl-*, *heptyl-*, and *octyl-chlorides*, have been given in the preceding table. *Myricyl chloride*, $CH_3[CH_2]_{28}CH_2Cl$, melts at 64°.

Methyl Bromide, CH_3Br—Monobrommethane.—Specific gravity is 1.73 at 0°.

Ethyl Bromide, C_2H_5Br, boils at 39°; its specific gravity is 1.47 at 13°. Bromine (6 pts.) is run into a mixture of red phosphorus (1 pt.) and 95 per cent. alcohol (6 pts.). The mixture should be chilled and constantly shaken while introducing the bromine. The reaction will be complete at the expiration of several hours. The ethyl bromide is then distilled off, washed first with a soda solution, then with water, and rectified after previous drying over calcium chloride. Ethyl bromide is the officinal *Æther bromatus.* It is prepared from potassium bromide and ethyl sulphuric acid (p. 139). It is used as a narcotic.

Propyl Bromide, C_3H_7Br, from the normal alcohol, boils at 71°; its specific gravity is 1.3520 at 20°.

Isopropyl Bromide, C_3H_7Br, from its corresponding alcohol, boils at 59.5°; its specific gravity is 1.3097 at 20°. It is most conveniently obtained by the action of bromine upon isopropyl iodide (B. **15**, 1904).

Upon boiling with aluminium bromide, or by heating to 250°, normal propyl bromide passes over into the isopropyl bromide (not completely, however) (B. **16**, 391). Such a transposition, due to displacement of the atoms in the molecule, occurs rather frequently, and is termed *molecular transposition.* It may be assumed that the normal propyl bromide, $CH_3 . CH_2 . CH_2 . Br$, at first breaks up into propylene, $CH_3 . CH : CH_2$ and HBr (see p. 91), which then, according to a common rule of addition (p. 93), unites with the propylene to isopropyl bromide, $CH_3 . CHBr . CH_3$. Similarly, isobutyl bromide, $(CH_3)_2 . CH . CH_2 . Br$, changes at 240° to tertiary butyl bromide, $(CH_3)_2 . CBr . CH_3$. The transpositions occurring on heating the halogen hydrides with the alcohols may be explained in the same manner.

The table already referred to also contains the boiling points of some of the higher homologues.

Cetyl Bromide, $CH_3[CH_2]_{14}CH_2Br$, melts at 15°.

On exposure to the air the iodides soon become discolored by deposition of iodine. The iodides of the secondary and tertiary alcohols are easily converted by heat into alkylens, C_nH_{2n} and HI. Consult A. **243**, 30, upon the specific volumes of the alkyl iodides.

Methyl Iodide, CH_3I, is a heavy, sweet-smelling liquid, boiling at 43°, and has a specific gravity of 2.19 at 0°. In the cold it unites with H_2O to form a crystalline hydrate, $2CH_3I + H_2O$.

Ethyl Iodide, C_2H_5I, is a colorless, strongly refracting liquid, boiling at 72° and having a specific gravity of 0.975 at 0°. It was discovered by Gay-Lussac in 1815. It is prepared similarly to ethyl bromide.

Propyl Iodide, C_3H_7I, from propyl alcohol, has a specific gravity of 1.7427 at 20°.

Isopropyl Iodide, C_3H_7I, is formed from isopropyl alcohol, propylene glycol, $C_3H_6(OH)_2$, or from propylene, and is most conveniently prepared by distilling a mixture of glycerol, amorphous phosphorus, and iodine (A. **138**, 364):

$$C_3H_5\,(OH)_3 + 5HI = C_3H_7I + 2I_2 + 3H_2O.$$

Here we have allyl iodide, $CH_2 = CH—CH_2I$, produced first (see below), and this is further changed to propylene, $CH_2 = CH—CH_3$, and isopropyl iodide.

Isopropyl Iodide boils at 89.5°, and has a specific gravity of 1.7033 at 20°.

The boiling points of some of the higher alkylogens will be found in the preceding table. *Cetyl iodide*, $CH_3 . [CH_2]_{14}CH_2I$, melts at 22°, and *myricyl iodide*, $CH_3[CH_2]_{28}CH_2I$, at 70°.

II. HALOID ESTERS OF THE UNSATURATED ALCOHOLS.

Only the haloid esters of the most important olefine and acetylene alcohols will be given; they are the **allyl haloids** and the **propargyl haloids**. The former are prepared from allyl alcohol by methods similar to those employed for the preparation of the corresponding compounds from ethyl alcohol. They are isomeric with the β- and α-haloid propylenes (p. 105), from which they are distinguished by their adaptability for double decompositions:

	Formula.	Boiling Point.	Sp. Gravity.
Allyl Fluoride (B. **24**, R. 40),	$CH_2 = CH . CH_2Fl$	—10°	. .
Allyl Chloride, ...	$CH_2 = CH . CH_2Cl$	46°	0.9379 (20°)
Allyl Bromide, ...	$CH_2 = CH . CH_2Br$	71°	1.461 (0°)
Allyl Iodide, ...	$CH_2 = CH . CH_2I$	101°	1.789 (16°)

The allyl haloids are liquids with leek-like odor. Allyl chloride, heated to 100° with HCl, yields propylene chloride, $CH_3 . CHCl . CH_2Cl$. Allyl bromide, heated to 100° with HBr, passes into trimethylene bromide, $CH_2Br . CH_2 . CH_2Br$. The addition of halogens produces glycerol trihaloid esters.

Allyl Iodide.—This is most frequently used. It is readily prepared from glycerol by the action of HI, or iodine and phosphorus.

It may be supposed that at first $CH_2I . CHI . CH_2I$ forms, but is subsequently decomposed into allyl iodide and iodine. (Preparation: A. **185**, 191; **226**, 206.) With excess of HI or phosphorus iodide, allyl iodide is further converted into propylene and isopropyl iodide (see above).

By continued shaking of allyl iodide (in alcoholic solution) with mercury, C_3H_5HgI separates in colorless leaflets (see mercury ethyl). Iodine liberates pure allyl iodide from this:

$$C_3H_5HgI + I_2 = C_3H_5I + HgI_2.$$

Alcoholic potash converts allyl iodide into allyl ethyl ether. With potassium sulphide it yields *allyl sulphide* (p. 150); with potassium sulphocyanide, *allyl sulphocyanide*, which passes readily into allyl mustard oil (see this). Allyl iodide has also been used in the synthesis of unsaturated alcohols.

Name.	Formula.	Boiling Point.	Sp. Gravity.
Propargyl Chloride (B. **8**, 398), .	$CH \equiv C . CH_2Cl$	65°	1.0454 (5°)
Propargyl Bromide (B. **7**, 761), .	$CH \equiv C . CH_2Br$	89°	1.5200 (20°)
Propargyl Iodide (B. **7**, 1132), .	$CH \equiv C . CH_2I$	115°	2.0177 (0°)

Propargyl chloride is produced when phosphorus trichloride acts upon propargyl alcohol.

B. ESTERS OF NITRIC ACID.

They are prepared by the interaction of alcohols and nitric acid. Nitrous acid is always produced. It is a consequence of oxidizing, secondary reactions, and may be destroyed by the addition of urea:

$$CO(NH_2)_2 + 2HNO_2 = CO_2 + 2N_2 + 3H_2O.$$

When much nitrous acid is present, it induces the decomposition of the nitric acid ester, and causes explosions.

Methyl Nitrate, $CH_3 . O . NO_2$, *Nitric Methyl Ester*, boils at 66°, and has a specific gravity, at 20°, of 1.182. When struck or heated to 150° it explodes very violently.

Ethyl Nitrate, $C_2H_5 . O . NO_2$, *Nitric Ethyl Ester.*

Ethyl nitrate is a colorless, pleasant-smelling liquid, boiling at 86°, and having a specific gravity of 1.112, at 15°. It is almost insoluble in water, and burns with a white light. It will explode if suddenly exposed to high heat. Heated with ammonia, it passes into ethylamine nitrate. Tin and hydrochloric acid convert it into hydroxylamine.

The *propyl ester*, $C_3H_7 . O . NO_2$, (B. **14**, 421) boils at 110°, the *isopropyl ester* at 101–102°, and the *isobutyl ester* at 123°.

C. ESTERS OF NITROUS ACID.

These are isomeric with the nitro-paraffins. The group NO_2 is present in both; while, however, in the nitro-compounds nitrogen is combined with carbon, in the esters the union is effected by oxygen:

$C_2H_5 . NO_2$	$C_2H_5 . O . NO.$
Nitro-ethane.	Nitrous Ethyl Ester.

The nitrous esters, as might be inferred from their different structure, decompose into alcohols and nitrous acid when acted on by alkalies. Similar treatment will not decompose the nitro-compounds. Nascent hydrogen (tin and hydrochloric acid) converts the latter into amines, while the esters are saponified.

Nitrous acid esters are produced in (1) the action of nitrous acid upon the alcohols; (2) by the action of alkyl iodides upon silver nitrite (B. **25**, R. 571). Nitro-paraffins, with high boiling points, are formed simultaneously.

Methyl Nitrite, Nitrous Methyl Ester, $CH_3 . O . NO$, boils at —12°.

Ethyl Nitrite, Nitrous Ethyl Ester, $C_2H_5 . O . NO$, is a mobile, yellowish liquid, of specific gravity 0.947, at 15°, and boils at +16°. It is insoluble in water, and possesses an odor resembling that of apples. It is obtained by the action of sulphuric acid and potassium nitrite upon alcohol (A. **253**, 251 *Anm.*). It is the active ingredient of *Spiritus ætheris nitrosi.*

When ethyl nitrite stands with water it gradually decomposes, nitrogen oxide being eliminated; an explosion may occur under some conditions. Hydrogen sulphide changes it into alcohol and ammonia.

Normal Butyl Nitrite, $C_4H_9 . O . NO$, boils at 75°, the **secondary** at 68°, and the **tertiary**, $C(CH_3)_3 . O . NO$, at 77°.

Isoamyl Nitrite, $C_5H_{11} . O . NO$, obtained by the distillation of fermentation amyl alcohol with nitric acid, is a yellow liquid boiling at 96°; its specific gravity is 0.902. An explosion takes place when the vapors are heated to 250°. Nascent hydrogen changes it into amyl alcohol and ammonia. Heated with methyl alcohol, it is transformed into methyl nitrite and amyl alcohol. The result is the same if ethyl alcohol be used (B. **20**, 656).

Amyl nitrite, "*Amylium nitrosum*," is used in medicine, and also for the preparation of nitroso- and diazo-compounds.

NOTE.—*Diazo-ethoxane*, $C_2H_5O . N = N — O . C_2H_5$, results from the interaction of ethyl iodide and nitrosyl silver $(NOAg)_2$. It is the ester of hyponitrous acid (B. **11**, 1630).

D. ESTERS OF SULPHURIC ACID.

(1) The *neutral esters* are formed by the action of the alkyl iodides upon silver sulphate, SO_4Ag_2; they are also produced, in slight quantity, on heating the primary esters or alcohols with sulphuric acid. They can be extracted with chloroform from the product, and are heavy liquids, soluble in ether, possess an odor like that of peppermint, and boil without decomposition. They will sink in water, and gradually decompose into a primary ester and alcohol:

$$SO_2<^{O.C_2H_5}_{O.C_2H_5} + H_2O = SO_2<^{O.C_2H_5}_{OH} + C_2H_5.OH.$$

The *Dimethyl Ester*, $SO_2(O.CH_3)_2$, boils at 188°. The *diethyl ester*, $SO_2(O.C_2H_5)_2$, boils at 208°. It is formed also from SO_3 and $(C_2H_5)_2O$, and when heated with alcohol, ethyl sulphuric acid and ethyl ether are produced (B. **13**, 1699; **15**, 947).

(2) The primary esters or **ether-acids** are produced (1) when the alcohols are mixed with concentrated sulphuric acid:

$$SO_2(OH)_2 + C_2H_5.OH = SO_2<^{O.C_2H_5}_{OH} + H_2O.$$

The reaction takes place only when aided by heat, and it is not complete, because the mixture always contains free sulphuric acid and alcohol (compare p. 137). The reaction does proceed to completion if the alcohol be dissolved in very little sulphuric acid, and SO_3 in the form of fuming sulphuric acid be then allowed to act upon the well-cooled solution (B. **28**, R. 31). To isolate the ether-acids, the product of the reaction is diluted with water and boiled with an excess of barium carbonate. In this way the unaffected sulphuric acid is thrown out as barium sulphate; the barium salts of the ether-acids are soluble and crystallize out when the solution is evaporated. To obtain the acids in a free state their salts are treated with sulphuric acid or the lead salts (obtained by saturating the acids with lead carbonate) may be decomposed by hydrogen sulphide, and the solution allowed to evaporate over sulphuric acid.

Even secondary alcohols, by careful cooling of the components, are capable of forming ether sulphuric acids—*e. g.*, ethyl propyl carbinol (B. **26**, 1203).

(2) The *ether acids* also result from the union of the alkylens with concentrated sulphuric acid.

Properties.—These acids are thick liquids, which cannot be distilled. They sometimes crystallize. They dissolve readily in water and alcohol, but are insoluble in ether.

(1) When boiled or warmed with water they break down into sulphuric acid and alcohol:

$$SO_2<^{O.C_2H_5}_{OH} + H_2O = SO_4H_2 + C_2H_5.OH.$$

(2) When distilled, they yield sulphuric acid and alkylens (p. 92).

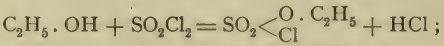
(3) Upon heating them with alcohols, simple and mixed ethers (p. 133) are produced.

They show a strongly acid reaction, and furnish salts which dissolve quite readily in water, and crystallize without great trouble. The salts gradually change to sulphates and alcohol when they are boiled with water. Those with the alkalies are frequently applied in different reactions. Thus with KSH and K_2S they yield mercaptans and thio-ethers (p. 149); with salts of fatty acids they furnish esters, and with KCN the alkyl cyanides, etc.

Methyl Sulphuric Acid, $SO_4(CH_3)H$, is a thick oil.

Ethyl Sulphuric Acid, $SO_4(C_2H_5)H$, is obtained by mixing 1 part alcohol with 2 parts concentrated sulphuric acid. The *potassium salt*, $SO_4(C_2H_5)K$, is anhydrous; it crystallizes in plates. The *barium* and *calcium* salts crystallize in large tablets with two molecules of H_2O each (A. **218**, 300).

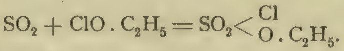
The *chlorides* or *chloranhydrides* of the ether sulphuric acids $\left(SO_2<^{O.C_2H_5}_{Cl}\right)$, called esters of chlorsulphonic acids, result in (1) the action of sulphuryl chloride upon the alcohols:



$$C_2H_5 . OH + SO_2Cl_2 = SO_2<\begin{matrix} O . C_2H_5 \\ Cl \end{matrix} + HCl\,;$$

Chloride of Ethyl
Sulphuric Acid.

(2) by the action of PCl_5 upon salts of the *ether acids;* (3) by the union of the olefines with $Cl . SO_3H$; (4) by the union of SO_3 with the alkyl chlorides; and (5) by the action of SO_2 upon the esters of hypochlorous acid (B. **19**, 860):



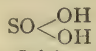
$$SO_2 + ClO . C_2H_5 = SO_2<\begin{matrix} Cl \\ O . C_2H_5. \end{matrix}$$

All are liquids with penetrating odor. Cold water decomposes them very slowly, with the formation of the ether acids. These they yield, together with ethyl chlorides, on adding alcohol to them. The reaction is rather energetic.

Chloride of Ethyl Sulphuric Acid, $C_2H_5 . O . SO_2Cl$, boils at about 152°. *Methyl Sulphuric Chloride*, $CH_3 . O . SO_2Cl$, boils at 132°.

E. ESTERS OF SYMMETRICAL SULPHUROUS ACID.

The empirical formula of sulphurous acid, SO_3H_2, may have one of two possible structures:



$$SO<\begin{matrix} OH \\ OH \end{matrix} \qquad \text{or} \qquad HSO_2 . OH.$$

Symm. Sulphurous Acid. Unsymm. Sulphurous Acid.

The ordinary sulphites correspond to formula 2, and it appears that in them one atom of metal is in direct combination with sulphur:

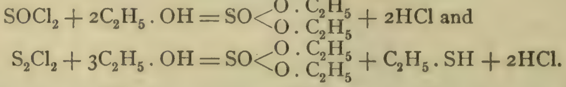
$Ag . SO_2 . OAg$ — Silver Sulphite.

$K . SO_2 . OH.$ — Prim. Pot. Sulphite.

Silver sulphite, $AgSO_2 . OAg$, when acted upon by ethyl iodide, yields the ethyl ester of ethyl sulphuric acid, $C_2H_5 . SO_3 . C_2H_5$, which splits off an ethyl group when treated with caustic potash, and yields ethyl sulphuric acid, $C_2H_5 . SO_3H$, the oxidation product of ethyl mercaptan, C_2H_5SH. The *sulpho-acids* and their esters, which must be viewed as esters of unsymmetrical sulphurous acid, will be described after the *mercaptans*.

Esters of Symmetrical Sulphurous Acid.

These are produced in the action of thionyl chloride, $SOCl_2$ (A. **111**, 93), or sulphur monochloride, S_2Cl_2, upon alcohols:



$$SOCl_2 + 2C_2H_5 . OH = SO<\begin{matrix} O . C_2H_5 \\ O . C_2H_5 \end{matrix} + 2HCl \text{ and}$$

$$S_2Cl_2 + 3C_2H_5 . OH = SO<\begin{matrix} O . C_2H_5 \\ O . C_2H_5 \end{matrix} + C_2H_5 . SH + 2HCl.$$

The mercaptan that is simultaneously formed sustains further decomposition. The sulphites thus produced are volatile liquids, insoluble in water, with an odor resembling that of peppermint, and decomposed by water, especially when heated, into alcohols and sulphurous acid.

Sulphurous Methyl Ester, $SO(O . CH_3)_2$, methyl sulphite, boils at 121°.

The **Ethyl Ester**, $SO(O.C_2H_5)_2$, boils at 161°. Its specific gravity at 0° is 1.106. PCl_5 converts it into the *chloride*, $SO<\begin{matrix}Cl\\O.C_2H_5\end{matrix}$, a liquid boiling at 122°, and decomposed by water into alcohol, SO_2 and HCl. It is isomeric with ethyl sulphonic chloride, $C_2H_5.SO_2Cl$ (p. 153). On mixing the ester with a dilute solution of the equivalent amount of KOH, a potassium salt, $SO.<\begin{matrix}O.C_2H_5\\OK\end{matrix}$, separates in glistening scales. This is viewed as a salt of the unstable ethyl sulphurous acid.

F. ESTERS OF HYPOCHLOROUS AND PERCHLORIC ACIDS.

The **Esters** of hypochlorous acid, ClOH, form on mixing concentrated aqueous solutions of hypochlorous acid with alcohol. They are unpleasantly-smelling, explosive liquids (B. **18**, 1767; **19**, 857). The perchloric acid esters are also explosive, and result from the action of ethyl iodide upon silver perchlorate.

Methyl Hypochlorite boils at 12°; **Ethyl Hypochlorite**, $ClOC_2H_5$, boils at 36°.

Sulphur dioxide converts these esters into chlorsulphonic esters (p. 146), while with KCN they yield *chlorimido-carbonic acid esters* (see these).

G. ESTERS OF BORIC ACID, ORTHO-PHOSPHORIC ACID, SYM. PHOSPHOROUS ACID, ARSENIC ACID, SYM. ARSENIOUS ACID, AND THE SILICIC ACIDS.

These esters are obtained by the action of BCl_3, $POCl_3$, PCl_3, $AsBr_3$, $SiCl_4$, Si_2OCl_6 upon alcohols and sodium alcoholates. Caustic alkalies saponify them with the production of alcohols and alkali salts of the respective inorganic acids. Most of them are decomposed entirely or in part by water.

Methyl Borate, $B(O.CH_3)_3$, boils at 65°.

Ethyl Borate, $B(O.C_2H_5)_3$, boils at 119°, and burns with a green-colored flame.

Triethyl Phosphoric Ester, $PO(O.C_2H_5)_3$, boils at 215 °.

Sym. Triethyl Phosphorous Ester, $P(O.C_2H_5)_3$, boils at 191°.

For the alkylized derivatives of unsymmetrical phosphorous and hypophosphorous acids—the **phospho-** and **phosphinic acids**—compare the **phosphines** and **phosphorus bases** (see these).

Triethyl Arsenic Ester, $AsO(O.C_2H_5)_3$, boils at 235°, and results from the interaction of silver arsenate and ethyl iodide.

Sym. Triethyl Arsenious Ester, $As(OC_2H_5)_3$, boils at 166°.

Compare *Arsenic bases* (see these) for arsenic derivatives corresponding to the *phospho-* and *phosphinic acids*.

Ethyl Ortho-silicic Ester, $Si(O.C_2H_5)_4$, boils at 165°; $Si(OCH_3)_4$, at 120–122°.

Ethyl Disilicic Ester, $Si_2O(O.C_2H_5)_6$, boils at 236°.

Ethyl Metasilicic Ester, $SiO(O.C_2H_5)_2$, boils at about 360°.

The silicic esters burn with a brilliant white flame. The ortho- and metasilicic esters correspond to the ortho- and meta- or ordinary carbonic acid esters: $C(OC_2H_5)_4$ and $CO(OC_2H_5)_2$.

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3. SULPHUR DERIVATIVES OF THE ALCOHOL RADICALS.

The sulphydrates and sulphides correspond to the metallic hydroxides and oxides, while the sulphur analogues of the alcohols and ethers are the *thio-alcohols* or *mercaptans* and *thio ethers* or *alkyl-*

sulphides, and the alkaline polysulphides find their analogues in the *alkyl polysulphides*:

$$\begin{array}{ccccc}
\left.\begin{matrix}H\\H\end{matrix}\right\}O; & \left.\begin{matrix}Na\\H\end{matrix}\right\}O; & \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O; & \left.\begin{matrix}Na\\Na\end{matrix}\right\}O; & \left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O \\
\left.\begin{matrix}H\\H\end{matrix}\right\}S; & \left.\begin{matrix}Na\\H\end{matrix}\right\}S; & \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}S; & \left.\begin{matrix}Na\\Na\end{matrix}\right\}S; & \left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}S \\
 & & \text{Ethyl Sulphydrate.} & & \text{Ethyl Sulphide.} \\
 & & & \left.\begin{matrix}Na\\Na\end{matrix}\right\}S_2; & \left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}S_2 \\
 & & & & \text{Ethyl Disulphide.}
\end{array}$$

A. **Mercaptans, Thio-alcohols, or Alkyl-sulphydrates.**—Although the mercaptans closely resemble the alcohols in general, the sulphur in them imparts additional specific properties. In the alcohols the H of OH is replaceable by alkali metals almost exclusively; in the mercaptans it can also be replaced by heavy metals. The mercaptans react very readily with mercuric oxide, to form crystalline compounds:

$$2C_2H_5 . SH + HgO = (C_2H_5 . S)_2Hg + H_2O.$$

Hence their designation as mercaptans (from *Mercurium captans*). The metal derivatives of the mercaptans are termed *mercaptides*.

The methods for their formation are:

(1) By the action of the alkylogens upon potassium sulphydrate in alcoholic solution:

$$C_2H_5Cl + KSH = C_2H_5 . SH + KCl.$$

(2) By distilling salts of the sulphuric esters with potassium sulphydrate or potassium sulphide (see p. 145):

$$SO_2{<}{}^{O\,.\,C_2H_5}_{OK} + KSH = C_2H_5 . SH + SO_4K_2.$$

The neutral esters of sulphuric acid—*e. g.*, $SO_2(O . C_2H_5)_2$ (p. 145)—also yield mercaptans when heated with KSH.

(3) A direct replacement of the oxygen of alcohols and ethers by sulphur may be attained by phosphorus sulphide:

$$5C_2H_5OH + P_2S_5 = 5C_2H_5 . SH + P_2O_5.$$

(4) By reduction of the chlorides of the sulphonic acids (see these):

$$C_2H_5 . SO_2Cl + 6H = C_2H_5SH + HCl + 2H_2O.$$

This reaction recalls the reduction of the acid chlorides to primary alcohols.

Properties and Transpositions of the Mercaptans.—The mercaptans are colorless liquids, mostly insoluble in water, and possess a disagreeable, garlic-like odor.

(1) Moderate oxidation with concentrated sulphuric acid, sulphuryl chloride, or iodine converts the mercaptans or mercaptides into disulphides (see these).

(2) When oxidized with nitric acid, the mercaptans yield the sulphonic acids. Conversely, the mercaptans result by the reduction of the sulphonic acids.

(3) By their union with aldehydes and ketones there result *mercaptals* and *mercaptols*,—*e. g.*, $CH_3CH(SC_2H_5)_2$, $(CH_3)_2C(SC_2H_5)_2$,—which will be treated at the conclusion of the aldehydes and ketones (see these).

Ethyl Mercaptan, $C_2H_5 . SH$, boils at 36°. Its specific gravity at 20° is 0.829. It is the most important and was the first discovered mercaptan (1834, Zeise, A. **11,** 1). Despite its fearful odor, it is technically made from ethyl chloride and potassium sulphydrate. It is used in the preparation of *sulphonal.* It is but slightly soluble in water; readily in alcohol and ether.

Mercury mercaptide, $(C_2H_5 . S)_2Hg$, crystallizes from alcohol in brilliant leaflets, melting at 86°, and is only slightly soluble in water. When mercaptan is mixed with an alcoholic solution of $HgCl_2$, the compound $C_2H_5 . S . HgCl$ is precipitated. The potassium and sodium compounds are best obtained by dissolving the metals in mercaptan diluted with ether; they crystallize in white needles.

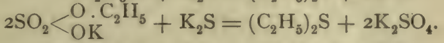
Methyl Mercaptan, CH_3SH, boils at + 6°; n-*propyl mercaptan* at 68°; *isopropyl mercaptan* at 59°; n-*butyl mercaptan* at 98°; *allyl mercaptan*, C_3H_5SH, at 90°.

n-*Butyl Mercaptan* is found in secretions of the stink-badger of the Philippines (Mydäus Marchei Huet) (Pharm. Centralhalle, 1896, No. 34).

B. **Sulphides or Thio-ethers.**—These are obtained like the mercaptans:

1. By the action of alkylogens upon potassium sulphide.
2. By distillation of salts of the ethyl sulphuric acids with potassium sulphide.
3. By the action of P_2S_5 upon ethers.
4. Upon heating the lead mercaptides:

1. $$2C_2H_5Cl + K_2S = (C_2H_5)_2S + 2KCl.$$

2. 

$$2SO_2{<}\begin{matrix}O . C_2H_5\\OK\end{matrix} + K_2S = (C_2H_5)_2S + 2K_2SO_4.$$

3. $$5(C_2H_5)_2O + P_2S_5 = 5(C_2H_5)_2S + P_2O_5.$$

4. $$(C_2H_5S)_2Pb = (C_2H_5)_2S + PbS.$$

Further, by the interaction of alkyl haloids and potassium on sodium mercaptides, when mixed thio-ethers are also produced:

5. $$C_2H_5SNa + C_2H_5I = (C_2H_5)_2S + NaI$$
$$C_2H_5SNa + C_3H_7I = C_2H_5 . S . C_3H_7 + NaI.$$

Methods 1, 2, and 5 are analogous to those used in the preparation of the corresponding ethers.

The sulphides, like the mercaptans, are colorless liquids, insoluble in water, but easily soluble in alcohol and ether. When impure their odor is very disagreeable, but quite ethereal when pure (B. 27, 1239).

Transpositions.—The sulphides are characterized by their additive power. (1) They unite with Br_2, and (2) with metallic chlorides—*e. g.*, $(C_2H_5)_2S . HgCl_2$, $[(C_2H_5)_2S]_2 PtCl_4$; (3) also with alkyl iodides to sulphine iodides (p. 150); (4) they are oxidized to sulphoxides (p. 159) and sulphones (p. 159) by nitric acid.

Methyl Sulphide, $(CH_3)_2S$, boils at 37.5°.

Ethyl Sulphide, $(C_2H_5)_2S$, boils at 91°.

n-*Propyl sulphide*, $(C_3H_7)_2S$, boils at 130–135°; n-*butyl sulphide* at 182°; *isobutyl sulphide* at 173°.

Cetyl Sulphide, $(C_{16}H_{33})_2S$, fuses at 57°.

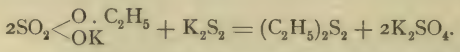
The sulphides of vinyl and allyl alcohols occur in nature. They are far more important than the sulphides of the normal alcohols. This is particularly true of allyl sulphide.

Vinyl Sulphide, $(C_2H_3)_2S$, is the principal ingredient of the oil of *Allium ursinum*, and is perfectly similar to allyl sulphide. It boils at 101°; its specific gravity is 0.9125. It forms $(C_2H_3Br_2)_2SBr_2$ with six atoms of bromine. Silver oxide changes it to vinyl ether, $(C_2H_3)_2O$ (p. 136) (A. **241**, 90).

Allyl Sulphide, $(C_3H_5)_2S$, is the chief constituent of the oil of garlic (from *Allium sativum*), and is obtained by the distillation of garlic with water (Wertheim, 1844). It occurs in many of the *Cruciferæ*. It may be prepared artificially by digesting allyl iodide with potassium sulphide in alcoholic solution. It is a colorless, disagreeable-smelling oil, but slightly soluble in water. It boils at 140°. It forms crystalline precipitates with alcoholic solutions of $HgCl_2$ and $PtCl_4$. With silver nitrate it yields the crystalline compound $(C_3H_5)_2S\,.\,2AgNO_3$.

Allyl mustard oil is produced on heating the mercury derivative with potassium sulphocyanide. Vinyl mustard oil is prepared in an analogous manner.

C. **Alkyl Disulphides** are produced (1) like the alkyl monosulphides upon distilling salts of the ethyl sulphuric acids or alkylogens with potassium disulphide; (2) by the action of iodine or concentrated sulphuric acid upon mercaptides; (3) by the action of sulphuryl chloride on the mercaptans:

1. 

$$2SO_2{<}\begin{matrix}O\,.\,C_2H_5\\OK\end{matrix} + K_2S_2 = (C_2H_5)_2S_2 + 2K_2SO_4.$$

2. $$2C_2H_5SK + I_2 = C_2H_5S{-}S{-}C_2H_5 + 2KI.$$

3. $$2C_2H_5SH + SO_2Cl_2 = (C_2H_5)_2S_2 + SO_2 + 2HCl.$$

When bromine acts upon a mixture of two mercaptans, mixed alkyl disulphides are produced (B. **19**, 3132). Nascent hydrogen reduces the alkyl disulphides to mercaptans, while zinc dust converts them into zinc mercaptides:

$$(C_2H_5)_2S_2 + Zn = (C_2H_5S)_2Zn.$$

Mercaptides result on heating them with potassium disulphide (B. **19**, 3129; compare also phenyl disulphide), and dilute nitric acid changes them to alkyl thiosulphonic esters (p. 153).

Methyl Disulphide, $(C_2H_3)_2S_2$, boils at 112°. *Ethyl Disulphide*, $(C_2H_5)_2S_2$, boils at 151°. They are oils with an odor like that of garlic.

D. **Sulphine or Sulphonium Compounds** (B. **27**, 505 *Anm.*). (1) The sulphides of the alcohol radicals (thio-ethers) combine with the iodides (also with bromides and chlorides) of the alcohol radicals at ordinary temperatures, more rapidly on application of heat, and form crystalline compounds:

$$(C_2H_5)_2S + C_2H_5I = (C_2H_5)_3\overset{IV}{S}I.$$

Triethyl Sulphonium Iodide.

These are perfectly analogous to the halogen derivatives of the strong basic radicals. By the action of moist silver oxide the halogen atom in them may be replaced by hydroxyl, and hydroxides similar to potassium hydroxide be formed:

$$(C_2H_5)_3SI + AgOH = (C_2H_5)_3S\,.\,OH + AgI.$$

(2) The sulphine or sulphonium haloids are also obtained on heating the sulphur ethers with the halogen hydrides, and (3) the alkyl sulphides with iodine (B. **25**, R. 641):

$$2(C_2H_5)_2S + HI = (C_2H_5)_3SI + C_2H_5SH$$
$$4(CH_3)_2S + I_2 = 2(CH_3)_3SI + (CH_3)_2S_2.$$

(4) The acid chlorides react similarly.

(5) By the action of methyl iodide on metallic sulphides:

$$SnS + 3CH_3I = SnI_2 + (CH_3)_3SI.$$

Often when the alkyl iodides act on the sulphides of higher alkyls the latter are displaced (B. **8**, 825).

$(C_2H_5)_2S \, . \, CH_3I$ and $\genfrac{}{}{0pt}{}{CH_3}{C_2H_5}{>}S \, . \, C_2H_5I$ are not isomeric, in which case a difference of the 4 valences of S would be proven, but identical (B. **22**, R. 648).

The sulphonium hydroxides are crystalline, efflorescent, strongly basic bodies, readily soluble in water. Like the alkalies, they precipitate metallic hydroxides from metallic salts, set ammonia free from ammoniacal salts, absorb CO_2 and saturate acids, with the formation of neutral salts:

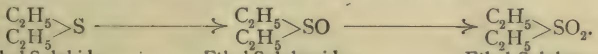
$$(C_2H_5)_3S \, . \, OH + NO_3H = (C_2H_5)_3S \, . \, NO_3 + H_2O.$$

We thus observe that relations similar to those noted with the nitrogen group prevail with sulphur (also with selenium and tellurium). Nitrogen and phosphorus combine with four hydrogen atoms (also with alcoholic radicals) to form the groups ammonium, NH_4, and phosphonium, PH_4, which yield compounds similar to those of the alkali metals. Sulphur and its analogues combine in like manner with three univalent alkyls, and give sulphonium and sulphine derivatives. Other non-metals and the less positive metals, like lead and tin, exhibit a perfectly similar behavior. By addition of hydrogen or alkyls they acquire a strongly basic, metallic character (see the metallo-organic compounds and also the aromatic iodonium bases).

Trimethyl Sulphonium Iodide, $(CH_3)_3SI$, is readily soluble in water, soluble with difficulty in alcohol, and crystallizes from the latter in white needles. At 215° it breaks down quietly into methyl sulphide and methyl iodide. Platinic chloride precipitates, from solutions of its chloride, a chloroplatinate, $[(CH_3)_3SCl]_2 \, . \, PtCl_4$, very similar to ammonium platinum chloride. **Trimethyl Sulphonium Hydroxide,** $(CH_3)_3SOH$, consists of deliquescent crystals with a strongly alkaline reaction.

Consult B. **24**, R. 906, upon the refractive power and the lowering of the freezing point of sulphine compounds.

E. **Sulphoxides** and **Sulphones,** as mentioned (p. 149), result from the oxidation of the sulphides with nitric acid:

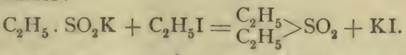


$$\genfrac{}{}{0pt}{}{C_2H_5}{C_2H_5}{>}S \longrightarrow \genfrac{}{}{0pt}{}{C_2H_5}{C_2H_5}{>}SO \longrightarrow \genfrac{}{}{0pt}{}{C_2H_5}{C_2H_5}{>}SO_2.$$

Ethyl Sulphide. Ethyl Sulphoxide. Ethyl Sulphone.

The *sulphoxides* may be compared to the ketones. Nascent hydrogen reduces them to sulphides. **Methyl- and Ethyl Sulphoxides** are thick oils, which combine with nitric acid: $(CH_3)_2SO \, . \, NO_3H$. Barium carbonate will liberate the sulphoxides from these salts. **Methyl Sulphoxide** is also formed when silver oxide acts upon *methyl sulph-bromide*, $(CH_3)_2SBr_2$.

The *sulphones*, obtained from the sulphoxides by means of nitric acid, or by oxidation with potassium permanganate, may also be regarded as esters of the alkyl sulphinic acids (see these), because they can be prepared from salts of the latter through the action of alkyl iodides:



$$C_2H_5 \, . \, SO_2K + C_2H_5I = \genfrac{}{}{0pt}{}{C_2H_5}{C_2H_5}{>}SO_2 + KI.$$

However, they are not true esters, but remarkable compounds, characterized by great stability, in which both alcohol radicals are linked to sulphur. They cannot be reduced to sulphides.

Methyl Sulphone, $(CH_3)_2SO_2$, melts at 109° and boils at 238°.
Ethyl Sulphone, $(C_2H_5)_2SO_2$, melts at 70° and boils at 248°.

ALKYL SULPHONIC ACIDS, ALKYL THIOSULPHURIC ACIDS, ALKYL THIOSULPHONIC ACIDS, AND ALKYL SULPHINIC ACIDS.

These compounds have the general formulas:

$R'.SO_2OH$	$R'S.SO_3H$	$R'.SO_2SH$	$R'.SO_2H$
$C_2H_5.SO_2OH$	$C_2H_5S.SO_3H$	$C_2H_5.SO_2SH$	$C_2H_5.SO_2H$
Ethyl Sulphonic Acid.	Ethyl Thiosulphuric Acid.	Ethyl Thiosulphonic Acid.	Ethyl Sulphinic Acid.

F. Sulphonic Acids.

The sulpho-acids or sulphonic acids contain the *sulpho-group* —$SO_2.OH$, joined to carbon. This is evident from their production by the oxidation of the mercaptans, and from their re-conversion into mercaptans (p. 148). They can be viewed as ester derivatives of the unsymmetrical sulphurous acid, HSO_2OH (p. 146).

Formation.—(1) Their salts result from the interaction of alkaline sulphites and alkyl iodides; their esters are formed when alkyl iodides act upon silver sulphite:

$$K.SO_2.OK + C_2H_5I = \underset{\text{Potassium Ethyl Sulphonate.}}{C_2H_5.SO_2OK} + KI$$

$$Ag.SO_2.OAg + 2C_2H_5I = \underset{\text{Ethyl Sulphonic Ethyl Ester.}}{C_2H_5.SO_2.O.C_2H_5} + 2AgI.$$

(2) By oxidation of (a) the mercaptans; (b) the alkyl disulphides; (c) the alkyl thiocyanates with nitric acid:

$$\left.\begin{matrix} C_2H_5SH \\ [C_2H_5S]_2 \\ C_2H_5S.CN \end{matrix}\right\} \xrightarrow{O} C_2H_5.SO_3H.$$

(3) The alkyl sulphinic acids are readily oxidized to sulphonic acids.

(4) The sulpho-acids can be formed further by the action of sulphuric acid or sulphur trioxide upon alcohols, ethers, and various other bodies. This reaction is very common with benzene derivatives and proceeds without difficulty.

Properties and Transpositions.—These acids are thick liquids, readily soluble in water, and generally crystallizable. They suffer decomposition when exposed to heat, but are not altered when boiled with alkaline hydroxides. When fused with solid alkalies they break up into *sulphites* and alcohols:

$$C_2H_5.SO_2.OK + KOH = KSO_2.OK + C_2H_5.OH.$$

PCl_5 changes them to chlorides,—*e. g.*, $C_2H_5.SO_2Cl$,—which become mercaptans through the agency of hydrogen, or by the action of sodium alcoholates pass into the neutral esters—$C_2H_5.SO_3.C_2H_5$ (p. 146).

Many of these reactions plainly indicate that in the sulphonic acids the sulphur is directly combined with the alkyls, and that very probably, therefore, in the sulphites the *one* metallic atom is directly united to sulphur. The sulphonic esters boil considerably higher than the esters of symmetrical sulphurous acid (p. 146). Alkalies convert the latter into sulphites and alcohol, whereas in the sulphonic esters only one alkyl group—that not directly linked to sulphur—is removed.

Methyl Sulphonic Acid, $CH_3.SO_3H$, was synthetically prepared by Kolbe in 1845 from carbon disulphide. Chlorine converted the latter into trichlormethyl sulphonic chloride, which was changed to the corresponding acid, and the latter reduced by sodium amalgam to methyl sulphonic acid, just as acetic acid is obtained from trichlor-acetic acid (see this) (A. **54**, 174):

$$C + 2S = CS_2 \longrightarrow CCl_3.SO_2Cl \longrightarrow CCl_3.SO_3H \longrightarrow CH_3.SO_3H.$$

Trichlormethyl sulphonic acid will be discussed later, after carbonic acid.

Barium Salt, $(CH_3.SO_3)_2Ba + \frac{1}{2}H_2O$. *Methyl Sulpho-chloride*, $CH_3.SO_2Cl$, boils at 160°.

Ethyl Sulphonic Acid, $C_2H_5 . SO_3H$, is oxidized by concentrated nitric acid to ethyl sulphuric acid, $C_2H_5O . SO_3H$ (p. 144).

Its *lead salt*, $(C_2H_5 . SO_3)_2Pb$, is readily soluble. Its *chloride*, $C_2H_5 . SO_2Cl$, boils at 177°. Its *methyl ester*, $C_2H_5SO_3CH_3$, boils at 198°. Its *ethyl ester*, $C_2H_5 . SO_3 . C_2H_5$, boils at 213.4°.

G. Alkyl Thiosulphuric Acids.

1. The well-crystallized alkali salts of these acids are made by acting upon alkaline hyposulphites with primary saturated alkyl iodides (B. 7, 646, 1157) or alkyl bromides (B. 26, 996):

$$C_2H_5I + NaS . SO_3Na = C_2H_5S . SO_3Na + NaI.$$

Sodium ethyl thiosulphate is called *Bunte's salt*, after its discoverer. (2) It also results when iodine acts upon a mixture of sodium mercaptide and sodium sulphite:

$$C_2H_5SNa + NaSO_3Na + I_2 = C_2H_5S . SO_3Na + 2NaI.$$

The free acids are not stable. Mineral acids convert sodium ethyl thiosulphate into mercaptan and primary sodium sulphate. Heat breaks down the salts into disulphides, neutral potassium sulphate, and sulphur dioxide.

H. The Alkyl Thiosulphonic Acids.

These acids are only stable in salts and esters. They are formed by the action of the chlorides of sulpho-acids upon potassium sulphide: $C_2H_5 . SO_2Cl + K_2S = KCl + C_2H_5 . SO_2 . SK$. The *esters*, $R . SO_2SR$, of this new class were formerly called *alkyl disulphoxides*, $R_2S_2O_2$, and are obtained (1) from the alkali salts by the action of the alkyl bromides (B. 15, 123): $C_2H_5 . SO_2 . SK + C_2H_5Br = C_2H_5 . SO_2 . SC_2H_5 + KBr$; and (2) by the oxidation of mercaptans and alkyl disulphides with dilute nitric acid: $(C_2H_5)_2S_2 + O_2 = C_2H_5 . SO_2 . SC_2H_5$. These esters are liquids, insoluble in water, and possessed of a disgusting onion-like odor (B. 19, 1241, 3131). **Ethyl Thiosulphuric Ethyl Ester**, $C_2H_5 . SO_2 . S . C_2H_5$, boils at 130°–140°.

I. Esters of Hydrosulphurous Acid—Sulphinic Acids. Two structural formulas are possible for hydrosulphurous acid: $H . \overset{IV}{SO} . OH$ and $\begin{matrix}H\\H\end{matrix}\!>\!\overset{VI}{SO_2}$. Replace one hydrogen atom and the sulphinic acids result, *e. g.*, (1) $C_2H_5 . \overset{IV}{SO} . OH$ or (2) $\begin{matrix}C_2H_5\\H\end{matrix}\!>\!\overset{VI}{SO_2}$.

The true alkyl sulphinic esters are derived from the first formula. The sulphones can be referred to the second formula (p. 151). The sulphinates are produced as follows:

(1) By the oxidation of the dry sodium mercaptides in the air.

(2) When SO_2 acts upon the zinc alkyls, the sulphinic acids (their zinc salts) result.

(3) When zinc acts upon the chlorides of the sulphonic acids:

(1) $C_2H_5SNa + 2O = C_2H_5SO_2Na$
(2) $(C_2H_5)_2Zn + 2SO_2 = [C_2H_5SO_2]_2Zn$
(3) $2C_2H_5SO_2Cl + 2Zn = [C_2H_5SO_2]_2Zn + ZnCl_2$.

The sulphones (p. 151) are produced in the action of alkyl iodides upon the alkaline sulphonates, while the *real esters* result from the etherification of the acids with alcohol and hydrochloric acid, or by the action of chlorcarbonic esters upon the sulphinates (B. 18, 2493): $R . SO_2Na + Cl . CO_2R = R . SO . OR + CO_2 + NaCl$. When these esters are saponified by alcohol or water they break down into alcohol and sulphinic acid, while the isomeric sulphones are not altered. The free sulphinic acids are liquids; not very stable; they rapidly oxidize to sulphonic acids. Potassium permanganate and acetic acid convert the sulphinic esters into sulphonic esters (B. 19, 1225), whereas the isomeric sulphones remain unchanged.

4. SELENIUM AND TELLURIUM COMPOUNDS.

These are perfectly analogous to the sulphur compounds.

Ethyl Hydroselenide, $C_2H_5 . SeH$, is a colorless, unpleasant-smelling, very mobile liquid. It combines readily with mercuric oxide to form a mercaptide.

Ethyl Selenide, $(C_2H_5)_2Se$, is a heavy, yellow oil, boiling at 108°. It unites directly with the halogens, *e. g.*, $(C_2H_5)_2SeCl_2$. It dissolves in nitric acid with formation of the oxide, $(C_2H_5)_2SeO$, which yields the salt, $(C_2H_5)_2Se(NO_3)_2$.

Tellurium mercaptans are not known. **Methyl Telluride,** $(CH_3)_2Te$, boils at 80–82°, and **Ethyl Telluride,** $(C_2H_5)_2Te$, boils at 137.5°. They are obtained by distilling barium alkyl sulphate with potassium telluride. They are heavy, yellow oils. The following compounds are derived from them: $(CH_3)_2Te(NO_3)_2$, $(CH_3)_2TeCl_2$, $(CH_3)_2TeO$, $(CH_3)_3TeI$, $(CH_3)_3Te . OH$, etc.

Dimethyl Tellurium Oxide, $(CH_3)_2TeO$, is a crystalline efflorescent compound. In properties it resembles CaO and PbO. It reacts strongly alkaline, expels ammonia from ammonium salts, and forms salts by neutralizing acids.

5. NITROGEN DERIVATIVES OF THE ALCOHOL RADICALS.

A. MONONITRO-PARAFFINS AND OLEFINES, HALOGEN MONONITRO-PARAFFINS.

By nitro-bodies are understood compounds of carbon in which the hydrogen combined with the latter is replaced by the univalent nitro-group, NO_2. The carbon is directly united to the nitrogen, as the reduction of the nitro-derivatives yields amido-compounds:

$$R'. NO_2 + 6H = R'. NH_2 + 2H_2O.$$

In the aromatic series the hydrogen atoms of the benzene nucleus are readily replaced by nitro-groups, *e. g.:*

$$C_6H_6 + NO_2OH = \underset{\text{Nitrobenzene.}}{C_6H_5NO_2} + H_2O.$$

Comparative refractometric investigations have shown that the nitro-group in nitroethane, and that in nitrobenzene, do not have the same structure (Z. ph. Ch. **6**, 552; compare p. 156). See B. **28**, R. 153, upon the heat of combustion of the nitro-paraffins.

(1) Fatty bodies can only be directly nitrated under certain conditions. This is particularly true when the substance contains a tertiary carbon atom, *e. g.*, $CHCl_3$, chloroform, or isovaleric acid, $(CH_3)_2CH . CH_2 . CO_2H$, etc. Normal hexane, normal octane, and paraffins richer in carbon have been nitrated by merely heating them to 130–140° with dilute nitric acid (Konowalow, B. **26**, R. 108; B. **28**, 1863).

(2) A common method for the preparation of the mononitro-derivatives of fatty hydrocarbons—the **nitroethanes**—consists in heating the iodides of the alcohol radicals with silver nitrite (*V. Meyer*, 1872) (A. **171**, 1; **175**, 88; **180**, 111):

$$C_2H_5I + AgNO_2 = C_2H_5 . NO_2 + AgI.$$

The isomeric esters of nitrous acid, such as $C_2H_5 . O . NO$, arise (B. 15, 1547) in this reaction. From this we would infer that silver nitrite conducted itself as if apparently consisting of $AgNO_2$ and $Ag . O . NO$. (Potassium nitrite does not act like $AgNO_2$.) Since, however, CH_3I only yields nitromethane, and the higher alkyliodides decompose more readily into alkylens, the greater the quantity of nitrous acid esters, it would appear that the formation of esters is influenced by the production of alkylens, which afterward form esters by the union with HNO_2 (A. 180, 157, and B. 9, 529). Possibly the alkylogens add themselves directly to the nitrogen, or in consequence of an opening-up of the double $N = O$ union.

(3) Simultaneously with the discovery of method 2, Kolbe demonstrated that nitromethane resulted from the action of potassium nitrite upon chlor-acetic acid. The first product in this instance was nitro-acetic acid, which broke down into carbon dioxide and nitromethane (J. pr. Ch. [2] 5, 427):

$$CH_2Cl . CO_2H \longrightarrow [CH_2(NO_2) . CO_2H] \longrightarrow CH_3NO_2 + CO_2.$$

(4) By a *nucleus-synthesis:* Zinc alkyls, acting upon chlor- and brom-nitroparaffins, produce mononitro-paraffins (B. 26, 129):

$$CH_3 . CHBrNO_2 \xrightarrow{Zn(CH_3)_2} CH_3 . CH(NO_2) . CH_3, \text{ Secondary Nitropropane.}$$

$$CCl_3 . NO_2 \xrightarrow{Zn(CH_3)_2} C . NO_2(CH_3)_3, \text{ Tertiary Nitrobutane.}$$

Properties and Transpositions of the Nitro-paraffins.—The nitroparaffins are colorless, agreeably-smelling liquids, which are sparingly soluble in water. They distil without decomposition, and only explode with difficulty. Their boiling points lie considerably higher than those of the corresponding nitrous esters (p. 144).

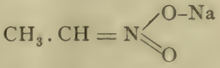
(1) Caustic potash and soda do not decompose the nitro-paraffins. They readily break down the isomeric nitrous esters (p. 144) into nitrous acid and alcohol. It is remarkable that the nitro-paraffins deport themselves like acids, thus differing from the halogen substitution products. An atom of hydrogen in them can be replaced by the action of caustic alkalies:

$$CH_3 . CH_2(NO_2) + KOH = CH_3 . CHK(NO_2) + H_2O.$$

The nitro-group always exerts such an acidifying influence upon the hydrogen in union with carbon. It is further increased by the entrance of halogen atoms or nitro-groups, but limits itself to the hydrogen atom united with the carbon atom carrying the nitro-group.

Thus the compounds: $CH_3 . CHBr(NO_2)$, brom-nitroethane, $CH_3 . CH(NO_2)_2$, di-nitroethane, $CH(NO_2)_3$, nitroform, etc., are strong acids, while $CH_3 . CBr_2(NO_2)$ and $(CH_3)_2C(NO_2)_2$, β-dinitro-propane, etc., possess neutral reaction and do not combine with bases. The acid properties diminish with increasing molecular weight. From aqueous solutions of the alkali salts, salts of heavy metals precipitate metallic compounds, which, as a rule, explode with great violence.

Nef assumes in the metal derivatives of the nitro-paraffins that the metal is combined with oxygen, *e.g.:*



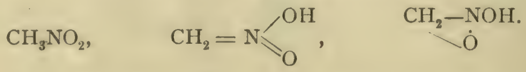
$$CH_3 . CH = N\begin{cases} O{-}Na \\ O \end{cases},$$

because they are resolved by acids into aldehydes or ketones and nitrous oxide. When carefully treated with acids, the nitro-paraffins can, in part, be regained from their metallic derivatives. It might be assumed, therefore, that the unstable (labile) bodies of the formula $RCH : N{\overset{\displaystyle /\!\!/ O}{\underset{\displaystyle \backslash OH}{}}}$ when liberated from their salts pass over into the more stable variety $R . CH_2 . NO_2$. The deportment of phenyl nitromethane renders this view probable; it occurs in the two isomeric modifications, $C_6H_5CH_2NO_2$ and $C_6H_5CH : N{\overset{\displaystyle /\!\!/ O}{\underset{\displaystyle \backslash OH}{}}}$ (B. **29**, 1223).

(2) By gradual reduction the nitro-bodies (V. Meyer, B. **24**, 3528, 4243; **25**, 1714) pass first into alkyl hydroxylamines (p. 172) and then into primary amines:

$$\underset{\text{Nitromethane.}}{CH_3NO_2} \xrightarrow{\qquad} \underset{\text{Methyl Hydroxylamine.}}{CH_3 . NH . OH} \xrightarrow{\qquad} \underset{\text{Methylamine.}}{CH_3NH_2.}$$

The conversion of nitro-paraffins into primary amines proves, as indicated before, that the nitrogen of the nitro-group present in them is linked to carbon. For nitromethane we have the choice between the following formulas (compare B. **29**, 2263):

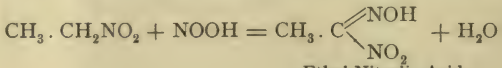


$$CH_3NO_2, \qquad CH_2 = N\begin{matrix}/OH\\ \backslash\!\!\backslash O\end{matrix}, \qquad \begin{matrix}CH_2—NOH.\\ \diagdown \dot{O}\end{matrix}$$

(3) The varying deportment of the nitro-paraffins with nitrous acid (better NO_2K and H_2SO_4) is very interesting, according as the nitro-group is linked to primary, secondary, or tertiary radicals.

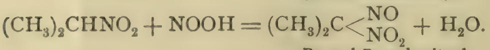
On mixing the primary nitro-compounds with a solution of NO_2K in concentrated potassium hydroxide and adding dilute H_2SO_4, the solution assumes in the beginning an *intense red* color due to a soluble, red-colored alkali salt of a **nitrolic acid.**

The nitro-compounds of the secondary radicals, when subjected to similar treatment, yield a *dark blue* coloration, due to a so-called **pseudo-nitrol**:



$$CH_3 . CH_2NO_2 + NOOH = CH_3 . C\begin{matrix}/\!\!/ NOH\\ \backslash NO_2\end{matrix} + H_2O$$

Ethyl Nitrolic Acid
(Nitro-acetoxime).



$$(CH_3)_2CHNO_2 + NOOH = (CH_3)_2C{<}{}^{NO}_{NO_2} + H_2O.$$

Propyl Pseudonitrol.

The nitro-compounds of tertiary radicals do not react with nitrous acid. Therefore, the preceding reactions serve as a very delicate and characteristic means of distinguishing primary, secondary, and tertiary alcoholic radicals (in their iodides), from one another.

(4) Chlorine and bromine, acting upon the alkali salts of primary and secondary nitro-paraffins, produce chlor- and brom-nitro-substitution products. In them the halogen atom is joined to the same carbon atom as the nitro-group.

For compounds resulting from the action of sodium ethylate and the alkyl iodides upon the nitro-ethanes, see B. **21**, R. 58 and 710.

Zinc ethide converts nitroethane into triethylamine oxide (B. **22**, R. 250).

Primary Mono-nitro-paraffins: Nitromethane, CH_3NO_2, boils at 101°. It is isomeric with formhydroxamic acid. *Sodium* and *potassium nitromethane* explode with great violence when they are heated. This also occurs when these substances, dried in a desiccator, come in contact with traces of water (B. **27**, 3406). When corrosive sublimate acts upon sodium nitromethane, fulminating mercury is produced (see this). By the action of caustic potash upon nitromethane or of hydroxylamine hydrochloride upon sodium nitromethane, *Methazonic Acid*, $C_2H_4N_2O_3$, is formed. It is a monobasic acid of unknown constitution (B. **29**, 2288), and melts at 79°.

Nitroethane, $CH_3.CH_2NO_2$, boils at 113–114°; *a-Nitropropane*, $CH_3.CH_2.CH_2NO_2$, boils at 130–131°; *Nitro-normal butane*, $CH_3.CH_2.CH_2.CH_2NO_2$, boils at 151°; *Nitro-isobutane*, $(CH_3)_2CH.CH_2NO_2$, boils at 137–140°; *Nitro-normal octane*, $CH_3.[CH_2]_6.CH_2.NO_2$, boils at 205–212°.

Secondary Mono-nitro-paraffins: Isonitropropane, $(CH_3)_2CHNO_2$, boils at 117–119°; *Secondary Nitrobutane*, $\genfrac{}{}{0pt}{}{C_2H_5}{CH_3}{>}CHNO_2$, boils at 138°.

Tertiary Mono-nitro-paraffins: Tertiary Nitrobutane, $(CH_3)_3C.NO_2$, boils at 126°.

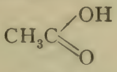
Halogen Nitro-compounds: Chlor-nitromethane, $CH_2Cl(NO_2)$, boils at 122°; *Brom-nitro-methane*, $CH_2Br(NO_2)$, boils at 146° (B. 29, 1823); *Brom-nitro-ethane*, $CH_3.CHBr(NO_2)$, boils at 146–147°; *a-brom-nitropropane*, $CH_3.CH_2.CHBr(NO_2)$, boils at 160–165°. All of these bodies are acids. The hydrogen of the $—CHCl(NO_2)$ or $—CHBr(NO_2)$ group is replaceable by the alkali metals.

Systematically considered, these derivatives belong to the aldehydes. It is only because of their genetic relations that they are described at the conclusion of the mono-nitro-paraffins. Thus, *β-brom-β-nitropropane*, $(CH_3)_2CBrNO_2$, boiling at 148–150°, belongs after acetone, while *dibrom-nitromethane*, $CHBr_2(NO_2)$ (B. 29, 1824), *dibrom-nitroethane*, $CH_3CBr_2(NO_2)$, boiling at 165°, and *dibrom-nitropropane*, boiling at 185°, should follow formic acid, acetic acid, and propionic acid. *Nitro-chloroform* or *chlorpicrin*, CCl_3NO_2, and *nitrobromoform*, or *brompicrin*, CBr_3NO_2, will be discussed after CCl_4, CBr_4, CI_4, together with carbonic acid.

The halogen atoms in the chlor- and brom-nitro-paraffins can be replaced by alcohol radicals through the action of zinc alkyls. Thus, higher homologous mono-nitro-paraffins can be prepared by nucleus-syntheses (p. 155).

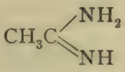
Nitropropylene, $CH_2=CH.CH_2NO_2$, from the action of allyl bromide or iodide upon silver nitrite, is a thick, brownish oil. It cannot be distilled without decomposition even under much diminished pressure. In every other respect it manifests the characteristic behavior of a primary nitro-body (B. 25, 1701).

NOTE.—*Nitrolic Acids* and *Pseudonitrols*.—These two classes of derivatives will be treated at this point, although the nitrolic acids belong after the mono-carboxylic acids, into which they readily pass, as well as the imido-amides or amidines and the amidoximes:



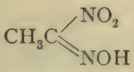
$$CH_3C{<}\genfrac{}{}{0pt}{}{OH}{O}$$

Acetic Acid.



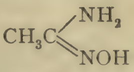
$$CH_3C{<}\genfrac{}{}{0pt}{}{NH_2}{NH}$$

Acetamidine.



$$CH_3C{<}\genfrac{}{}{0pt}{}{NO_2}{NOH}$$

Ethyl-nitrolic Acid.



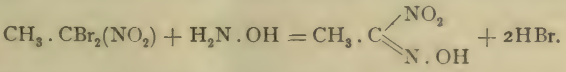
$$CH_3C{<}\genfrac{}{}{0pt}{}{NH_2}{NOH}$$

Ethenyl Amidoxime.

Systematically considered, the pseudonitrols should follow the ketones. They arise from their oximes, and are probably to be regarded as their nitric acid esters:

$$\underset{\text{Acetone.}}{(CH_3)_2CO}\qquad \underbrace{(CH_3)_2C{<}\genfrac{}{}{0pt}{}{NO_2}{NO}\qquad (CH_3)_2C=N.ONO_2}_{\text{Propyl Pseudonitrol.}}\qquad \underset{\text{Acetoxime.}}{(CH_3)_2C=NOH}$$

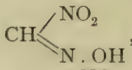
Nitrolic Acids.—They are produced (1) by the action of nascent nitrous acid upon the primary nitro-paraffins. (2) By treating the dibrom-nitro-paraffins with hydroxylamine:

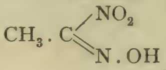


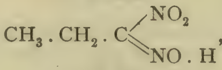
$$CH_3.CBr_2(NO_2)+H_2N.OH=CH_3.C{<}\genfrac{}{}{0pt}{}{NO_2}{N.OH}+2HBr.$$

Therefore they are to be regarded as nitro-oximes.

The nitrolic acids are solid, crystalline, colorless, or faintly-yellow colored bodies, soluble in water, alcohol, ether, and chloroform. They are strong acids, and form salts with alkalies which are not very stable, yielding at the same time a *dark red color*. They are broken up into hydroxylamine and the corresponding fatty acids, by tin and hydrochloric acid. When heated with dilute sulphuric acid they split up into oxides of nitrogen and *fatty acids*. They yield their esters when treated with acid chlorides (B. **27**, 1600; **29**, 1218).

Methyl Nitrolic Acid,  $CH\genfrac{}{}{0pt}{}{\diagup NO_2}{\diagdown N.OH}$, fuses at 64°.

Ethyl Nitrolic Acid,  $CH_3.C\genfrac{}{}{0pt}{}{\diagup NO_2}{\diagdown N.OH}$, melts at 81–82°.

Propyl Nitrolic Acid,  $CH_3.CH_2.C\genfrac{}{}{0pt}{}{\diagup NO_2}{\diagdown NO.H}$, melts at 60°, with decomposition.

Pseudonitrols.—The pseudonitrols, isomeric with the nitrolic acids, are formed (1) by the action of nitrous acid upon the secondary nitro-paraffins (see p. 156):

$$\underset{\text{Isonitro-propane.}}{(CH_3)_2CH(NO_2)} + NO.OH = (CH_3)_2C<\genfrac{}{}{0pt}{}{NO_2}{NO} + H_2O.$$

They are to be viewed as nitro-nitroso compounds. They are more easily produced (2) by the action of N_2O_4 upon ketonoximes (see these) (B. **21**, 507):

$$4(CH_3)_2C:N.OH + 3N_2O_4 = 4(CH_3)_2C<\genfrac{}{}{0pt}{}{NO_2}{NO} + 2H_2O + 2NO.$$

They are, in all probability, the nitric acid esters of the acetoximes, $(CH_3)_2C = N.O.NO_2$ (B. **21**, 1294).

The pseudonitrols are crystalline bodies with pungent odor, colorless in the solid condition, but exhibiting a *deep blue color* when fused or dissolved (in alcohol, ether, chloroform). They show a neutral reaction, and are insoluble in water, alkalies, and acids. Dissolved in glacial acetic acid, they are oxidized by chromic acid to *dinitro-compounds*.

When reduced by hydroxylamine in alkaline solution, they are changed to ketoximes (B. **29**, 88, 98):

$$(CH_3)_2.C<\genfrac{}{}{0pt}{}{NO_2}{NO} \longrightarrow (CH_3)_2C = N.OH.$$

Propyl Pseudonitrol, $(CH_3)_2C<\genfrac{}{}{0pt}{}{NO_2}{NO}$, nitro-nitroso-propane, melts at 76°.

Butyl Pseudonitrol, $\genfrac{}{}{0pt}{}{C_2H_5}{CH_3}>C<\genfrac{}{}{0pt}{}{NO_2}{NO}$, melts at 58°. Consult B. **29**, 94, for higher homologues.

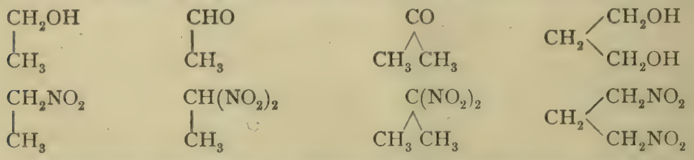
Dinitro-paraffins.—There are three classes of dinitro-paraffins. The two nitro-groups are joined—

(1) to one terminal carbon atom: ω_2-*dinitro-paraffins* or primary dinitro-compounds;

(2) to an intermediate carbon atom: *meso-dinitro-paraffins* or secondary dinitro-compounds;

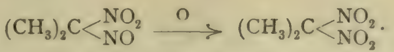
(3) to two different carbon atoms.

These three classes, according to the position of the groups, bear the same relations to aldehydes, ketones, and glycols as the mono-nitro-paraffins sustain to the alcohols:



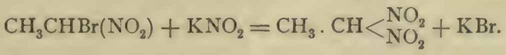
Notwithstanding these points of relationship, it is practicable to discuss the dinitro-paraffins after the pseudonitrols.

Formation.—(1) By the oxidation of the pseudonitrols with chromic acid *meso-dinitro-paraffins* are produced:



$$(CH_3)_2C{<}^{NO_2}_{NO} \xrightarrow{O} (CH_3)_2C{<}^{NO_2}_{NO_2}.$$

(2) They result from the interaction of potassium nitrite and the brom-nitro-paraffins:



$$CH_3CHBr(NO_2) + KNO_2 = CH_3 . CH{<}^{NO_2}_{NO_2} + KBr.$$

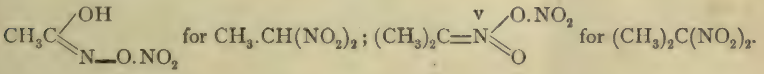
(3) By the action of concentrated nitric acid upon—
(*a*) secondary alcohols,
(*b*) ketones,
(*c*) mono-alkylized aceto-acetic esters,
the carbon chain is torn asunder and ω_2-*dinitro-paraffins* are formed:

$$\begin{aligned}(C_2H_5)_2CHOH &\longrightarrow CH_3 . CH_2 . CH(NO_2)_2 + CH_3 . CO_2H\\ (C_2H_5)_2CO &\longrightarrow CH_3 . CH_2 . CH(NO_2)_2 + CH_3 . CO_2H\\ CH_3CO . CH(C_2H_5)CO_2C_2H_5 &\longrightarrow CH_3 . CH_2 . CH(NO_2)_2 + CH_3 . CO_2H + CO_2.\end{aligned}$$

(4) By the oxidation of saturated mono-carboxylic acids, containing a tertiary carbon atom, with nitric acid: isobutyric and isovaleric acids yield *meso-dinitro-propane:*

$$(CH_3)_2CHCO_2H \qquad (CH_3)_2CH . CH_2 . CO_2H \longrightarrow (CH_3)_2C(NO_2)_2.$$

The primary dinitro-bodies are acids. The primary and secondary classes split off hydroxylamine when they are reduced with tin and hydrochloric acid. The former yield, at the same time, mono-carboxylic acids, and the latter ketones. This deportment led to the consideration of the following structural formulas for the two classes of dinitro-derivatives (B. **23**, 3494):



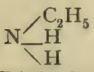
1,1-*Dinitroethane*, $CH_3 . CH(NO_2)_2$, boils at 185–186°; 1,1-*Dinitropropane*, $CH_3 . CH_2 . CH(NO_2)_2$, boils at 189°. 1, 1-*Dinitrohexane* boils at 212°. 2,2-*Dinitropropane*, $CH_3 . C(NO_2)_2 . CH_3$, melts at 53° and boils at 185.5°. 2,2-*Dinitrobutane*, $CH_3 . CH_2 . C(NO_2)_2 . CH_3$, boils at 199°. Higher homologues, see B. **29**, 95. The only ω-, ω'-, or 1,3-*Dinitropropane*, $NO_2CH_2 . CH_2 . CH_2NO_2$, having the two nitro-groups attached to different carbon atoms, is an unstable oil obtained by the action of $AgNO_2$ upon trimethylene iodide (B. **25**, 2638).

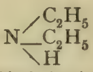
Of the poly-nitro-derivatives of methane there remain *nitroform*, $CH(NO_2)_3$, to be considered after chloroform, bromoform, and iodoform in connection with formic acid, *bromnitroform*, $C(NO_2)_3Br$, and *tetranitromethane*, $C(NO_2)_4$, which will come up for consideration under carbonic acid, following chlorpicrin and brompicrin.

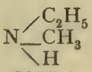
B. ALKYLAMINES AND ALKYL AMMONIUM DERIVATIVES.

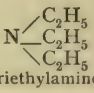
Alkylamines are those bodies which result from the introduction of univalent alkyls into ammonia for its hydrogen.

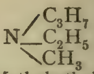
One, two, and three hydrogen atoms of the ammonia molecule may suffer this replacement, thus yielding the *primary*, *secondary*, and *tertiary* amines:


Ethylamine.


Diethylamine.


Methyl Ethylamine.


Triethylamine.


Methyl-ethyl-propylamine.

These are also sometimes called amide, imide, and nitrile bases. Under the imide and nitrile bases, the secondary and tertiary amines, we distinguished *simple* amines, those with similar alcohol radicals, and *mixed* amines, those containing different alcohol radicals; compare *simple* and *mixed* ethers (p. 132). Derivatives also exist which correspond to the ammonium salts and hypothetical ammonium hydroxide, NH_4OH:

$$(C_2H_5)_4\overset{v}{N}Cl \qquad (C_2H_5)_4\overset{v}{N}.OH$$

Tetraethyl Ammonium Chloride. Tetraethyl Ammonium Hydroxide.

These are the quaternary alkyl ammonium compounds.

Isomerism of the Alkylamines.—The isomerism of the simple alkylamines depends upon the homology of the alcohol radicals, *metamerism;* and in the higher alkylamines, in addition, upon the different position of the nitrogen in the same carbon chain, *isomerism of position;* and also upon the different manner of linkage of the carbon atoms of the isomeric alkyl residues, *nucleus isomerism* (p. 41).

There are seven isomerides of $C_4H_{11}N$:

$$N\left\{\begin{array}{l}C_4H_9\\H\\H\end{array}\right. \qquad N\left\{\begin{array}{l}C_3H_7\\CH_3\\H\end{array}\right. \qquad N\left\{\begin{array}{l}C_2H_5\\CH_3\\CH_3\end{array}\right.$$

4-Isomeric Butylamines. 2-Isomeric Propylmethylamines. Ethyl-dimethyl Amine.

History.—The existence of alkylamines, or alcohol bases, was very definitely predicted by Liebig in 1842 (Hdw. 1, 689). In 1849 Würtz discovered a method for the preparation of *primary amines.* It consisted in decomposing isocyanic ether with caustic potash. This was a discovery of the greatest importance for the development of organic chemistry. Shortly after, in 1849, A. W. Hofmann, by the action of alkylogens on ammonia, discovered a reaction which made possible the preparation of all the classes described in the preceding paragraphs: *primary*, *secondary*, *tertiary amines*, and the *alkyl ammonium bases.* This afforded the experimental basis for the introduction of the *ammonia type* into organic chemistry (compare p. 35). Since that time numerous other methods of preparation have been found, particularly for the primary amines.

The following general methods are the most important for preparing the above compounds:

(1 *a*) The iodides, the bromides, or the chlorides of the alcohol radicals are heated to 100°, in sealed tubes, with alcoholic ammonia (*A. W. Hofmann*, 1849). Two reactions occur here: first, the alkylogens combine with the ammonia, forming alkyl ammonium salts, which then are partially decomposed by *excess* of ammonia, with the

production of alkylamines, to which alkylogens again unite themselves—*e. g.*:

$$\begin{aligned}
NH_3 + C_2H_5I &= NH_2(C_2H_5)HI \xrightarrow{NH_3} NH_2C_2H_5 + NH_4I \\
NH_2C_2H_5 + C_2H_5I &= NH(C_2H_5)_2HI \xrightarrow{NH_3} NH(C_2H_5)_2 + NH_4I \\
NH(C_2H_5)_2 + C_2H_5I &= N(C_2H_5)_3HI \xrightarrow{NH_3} N(C_2H_5)_3 + NH_4I \\
N(C_2H_5)_3 + C_2H_5I &= N(C_2H_5)_4I.
\end{aligned}$$

The final product consists of the hydro-iodides of primary, secondary, and tertiary amines, and of the amide, imide, and nitrile bases, as well as the quaternary ammonium compounds. The amines are best obtained on a large scale by the action of ammonia upon the alkyl bromides (B. **22**, 700).

Potassium and sodium hydroxides decompose the salts of the amine, imide, and nitrile bases, with the splitting-off of the free bases, whereas the quaternary tetra-alkyl ammonium salts are *not* decomposed by caustic alkalies, and can thus be easily separated from the primary, secondary, and tertiary amines (B. **20**, 2224).

It is remarkable that the primary and secondary (B. **22**, R. 343) alkyl iodides yield at the same time secondary and tertiary amines, while the tertiary alkyl iodides do not form amines, but split off hydrogen iodide and pass into olefines.

(1 *b*) The *esters of nitric acid*, when heated to 100° with alcoholic ammonia, react in a manner analogous to the alkyl iodides:

$$C_2H_5 . O . NO_2 + NH_3 = C_2H_5 . NH_2 + HNO_3.$$

This reaction is often very convenient for the preparation of the primary amines (B. **14**, 421).

(1 *c*) *Tertiary amines* are produced when primary and secondary bases are heated with an excess of potassium methyl sulphate (B. **24**, 1678):

$$(C_2H_5)_2NH + CH_3OSO_3K = (C_2H_5)_2NCH_3 + HOSO_3K.$$

(1 *d*) Mono-, di-, and tri-alkylamines are obtained by directly heating the alcohols to 250–300° with zinc-ammonium chloride (B. **17**, 640).

(2) By action of nascent hydrogen (HCl and Zn) upon the nitro-paraffins (p. 156), when the alkyl hydroxylamines appear as *intermediate* products, and upon the halogen mono-nitro-paraffins:

$$\begin{aligned}
CH_3NO_2 + 4H &= CH_3NHOH + H_2O. \\
CH_3 . NO_2 + 6H &= CH_3 . NH_2 + 2H_2O. \\
CCl_3NO_2 + 12H &= CH_3NH_2 + 2H_2O + 3HCl.
\end{aligned}$$

This method is particularly important in the manufacture of commercially valuable primary amines—*e. g.*, aniline—from the readily accessible aromatic nitro-bodies. Zinin discovered the method when investigating the reduction of nitrobenzene, $C_6H_5NO_2$. V. Meyer applied it to the aliphatic nitro-derivatives.

(3 *a*) By the action of sodium in absolute alcohol upon the *aldehyde-alkylimides* (B. **29**, 2110); (3 *b*) when zinc dust and hydrochloric acid are allowed to act upon aldehyde-ammonia derivatives (B. **27**, R. 437); (3 *c*) from the *phenylhydrazones* (Tafel), and (3 *d*) the *oximes* (Goldschmidt) of the aldehydes and ketones by means

of sodium amalgam and glacial acetic acid (B. **19**, 1925, 3232; **20**, 505; **22**, 1854):

$$(CH_3)_2CH . CH = N(CH_3) + 2H = (CH_3)_2CH . CH_2 . NHCH_3$$
$$(CH_3) . CH : N—NH . C_6H_5 + 4H = CH_3 . CH_2NH_2 + C_6H_5NH_2$$
$$(CH_3)_2C : N—NH . C_6H_5 + 4H = (CH_3)_2CHNH_2 + C_6H_5NH_2$$
$$(CH_3)_2C : N—OH + 4H = (CH_3)_2CHNH_2 + H_2O.$$

Reaction 3 *a* yields secondary amines, while 3 *b*, 3 *c*, and 3 *d* afford primary amines.

(4) By the action of nascent hydrogen (from alcohol and sodium, B. **18**, 2957; **19**, 783; **22**, 1854) upon the *nitriles* or *alkyl cyanides* (Mendius, A. **121**, 129):

$$HCN + 4H = CH_3NH_2; \quad CH_3 . CN + 4H = CH_3 . CH_2 . NH_2.$$

Methylamine. Acetonitrile. Ethylamine.

The reaction constitutes an important intermediate factor both in the synthesis of alcohols (p. 113) and of amines.

(5) Warm the isocyanides of the alkyls, the isonitriles, or carbylamines with dilute hydrochloric acid; formic acid will split off (*A. W. Hofmann*):

$$C_2H_5 . NC + 2H_2O = C_2H_5 . NH_2 + CH_2O_2.$$

(6 *a*) The esters of *isocyanic* or *isocyanuric acid* are distilled with potassium hydroxide (*Würtz*, 1848):

$$CO : N . CH_3 + 2KOH = NH_2 . CH_3 + CO_3K_2.$$

Cyanic acid is changed to ammonia in precisely the same manner:

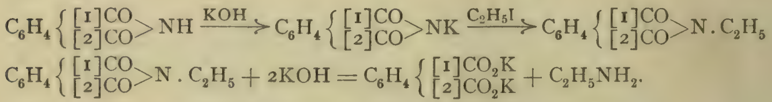
$$CO : NH + 2KOH = NH_3 + CO_3K_2.$$

To convert alcohol radicals into corresponding amines, the iodides are heated together with silver cyanate; the product of the reaction is then mixed with pulverized caustic soda, and distilled in an oil bath (B. **10**, 131).

(6 *b*) The *isothiocyanic esters* or the *mustard oils*, etc., are also broken down into primary amines by heating with water or dilute acids:

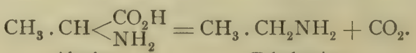
$$CS : N . C_2H_5 + 2H_2O = CO_2 + H_2S + C_2H_5NH_2.$$

(6 *c*) The isocyanic esters and the isothiocyanic esters or mustard oils are alkyl derivatives of the imide of carbonic acid, and thiocarbonic acid. The alkyl compounds of the *imide* of *o-phthalic acid* (see this) have shown themselves to be well adapted for the preparation of primary amines. They are readily prepared by acting upon potassium phthalimide with alkyl iodides. When heated with potassium hydroxide or acids, they separate into phthalic acid and primary amines (Gabriel, **20**, 2224; **24**, 3104):



$$C_6H_4\left\{\begin{matrix}{[1]}CO\\ {[2]}CO\end{matrix}\right.\!\!>NH \xrightarrow{KOH} C_6H_4\left\{\begin{matrix}{[1]}CO\\ {[2]}CO\end{matrix}\right.\!\!>NK \xrightarrow{C_2H_5I} C_6H_4\left\{\begin{matrix}{[1]}CO\\ {[2]}CO\end{matrix}\right.\!\!>N . C_2H_5$$
$$C_6H_4\left\{\begin{matrix}{[1]}CO\\ {[2]}CO\end{matrix}\right.\!\!>N . C_2H_5 + 2KOH = C_6H_4\left\{\begin{matrix}{[1]}CO_2K\\ {[2]}CO_2K\end{matrix}\right. + C_2H_5NH_2.$$

(7) By the distillation of amin- or amido-acids, especially with baryta:



$$CH_3 . CH<\begin{matrix}CO_2H\\ NH_2\end{matrix} = CH_3 . CH_2NH_2 + CO_2.$$

Alanine. Ethylamine.

(8) The splitting up of the secondary and tertiary aromatic p-nitroso-amines into salts of *nitrosophenol* (see this), by means of caustic potash, affords a means of preparing primary and secondary amines; p-nitro-sod-dimethyl aniline yields dimethyl amine:

$$NO[4]C_6H_4[1]N(CH_3)_2 + KOH = NH(CH_3)_2 + NO[4]C_6H_4[1]OK.$$

(9) The conversion of the amides of the monocarboxylic acids, by means of caustic potash and bromine, into amines, containing an atom less of carbon (A. W. Hofmann, B. **18**, 2734; **19**, 1822).

This reaction constitutes an intermediate step in the break-down of the saturated monocarboxylic acids, because the primary amines can be changed to alcohols, and the latter be oxidized to carboxylic acids, containing an atom less of carbon than the fatty acids, whose amides constituted the starting-out material.

The reaction proceeds in two phases, the first of which is the formation of the *brom-amide* of the fatty acid, and the second step the conversion of this new derivative into the primary amine:

$$C_2H_5 . CO . NH_2 + Br_2 + KOH = C_2H_5 . CO . NHBr + KBr + H_2O$$
$$C_2H_5 . CO . NHBr + 3KOH = C_2H_5 . NH_2 + CO_3K_2 + KBr + H_2O.$$

When 1 molecule of bromine and 2 molecules of the amide react, the product consists of *mixed ureas;* thus acetamide yields methyl aceto-urea.

The fatty-acid amides, with more than 5 C-atoms, not only yield amines, but also large quantities of the nitriles of the next lower acids:

$$C_8H_{17} . CO . NH_2 \quad \text{yields} \quad C_7H_{15} . CN.$$

(10) From acid-azides and alcohol. The corresponding acid is converted into an ester, the oxyethyl group is then replaced with $(NH . NH_2)$ by means of hydrazine hydrate, the acid-azide, $R . CO . NH . NH_2$, is changed by nitrous acid into the azide $R . CO . N_3$, the latter is boiled with water or alcohol, and the resulting urea or urethane acted upon with concentrated hydrochloric acid, when the alkylized base splits off (Curtius, B. **27**, 779; **29**, 1166).

$$R . CO . N_3 \xrightarrow{C_2H_5OH} R . NH . CO . ON_2H_5 \xrightarrow{HCl} R . NH_2.$$

Properties and Transpositions of the Amines.—The amines are very similar to ammonia in their deportment. The lower members are gases, with ammoniacal odor, and are very readily soluble in water; their combustibility distinguishes them from ammonia. This was the property that attracted Würtz to ethylamine (B. **20**, R. 928). The higher members are liquids, readily soluble in water, and only the highest are sparingly soluble. Many amines possess the power of forming hydrates with water, accompanied by very considerable rise in temperature. They can be dried over potashes. Most of the oily hydrates contain a molecule of water for each nitrogen atom. This can only be removed by means of caustic potash (B. **27**, R. 579), or by distillation over barium oxide. Like ammonia, they unite directly with acids to form salts, which differ from ammoniacal salts by their solubility in alcohol. They combine with some metallic chlorides, and form compounds perfectly analogous to the ammonium double salts; *e. g.*—

$$[N(CH_3)H_3Cl]_2PtCl_4. \quad N(CH_3)H_3Cl \,.\, AuCl_3. \quad [N(CH_3)_3HCl]_2HgCl_2.$$

The ammonia in the alums, the cuprammonium salts and other compounds may be replaced by amines.

Their basicity is greater than that of ammonia, and increases with the number of alkyls introduced (J. pr. Ch. [2] **33**, 352).

The reactivity of the primary and secondary amines, as compared with the tertiary amines, is dependent upon the ease with which the ammonia hydrogen atoms, not substituted by alcohol radicals, are replaced; hence, the primary and the secondary amines in many reactions behave like ammonia.

A primary amine is distinguished from a secondary amine, and this from a tertiary amine, by treating the amine alternately with methyl iodide and caustic potash until all the hydrogen atoms in the ammonia present are replaced by methyl groups. Whether the latter have entered, and what their number may be, is most conveniently determined by the analysis of the platinum double chloride of the base previous to and after the action of the methyl iodide. If two methyl groups have entered, then the amine was primary; if one methyl group has entered, then the base was secondary; and should the base remain unchanged, then it is tertiary in its character.

Tertiary, secondary, and primary amines may also be obtained by the dry distillation of the halogen salts of the ammonium bases:

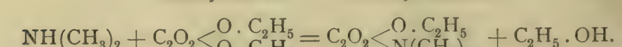
$$\begin{aligned} N(CH_3)_4Cl &= N(CH_3)_3 + CH_3Cl \\ N(CH_3)_3HCl &= NH(CH_3)_2 + CH_3Cl \\ NH(CH_3)_2HCl &= NH_2(CH_3) + CH_3Cl, \text{ etc.} \end{aligned}$$

These reactions serve for the commercial production of methyl chloride from trimethylamine.

Primary and secondary amines show the following reactions:

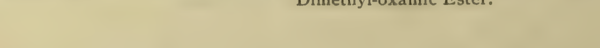
(1) Primary and secondary amines, like ammonia, are transposed by acid esters, with the formation of mono- and di-alkylized acid amides (see these) and alcohols. A. W. Hofmann based a method for the separation of primary, secondary, and tertiary amines upon their deportment toward diethyl oxalate (B. **8**, 760).

The mixture of the dry bases is treated with diethyl oxalate, when the primary amine, *e. g.*, methylamine, is changed to diethyl oxamide, which is soluble in water; dimethylamine is converted into the ester of dimethyl oxamic acid (see oxalic acid compounds); and trimethylamine is not acted upon:



$$2NH_2(CH_3) + C_2O_2\left\langle\begin{matrix} O \,.\, C_2H_5 \\ O \,.\, C_2H_5 \end{matrix}\right. = C_2O_2\left\langle\begin{matrix} NH \,.\, CH_3 \\ NH \,.\, CH_3 \end{matrix}\right. + 2C_2H_5 \,.\, OH$$

Diethyl-oxalate. Dimethyl-oxamide.



$$NH(CH_3)_2 + C_2O_2\left\langle\begin{matrix} O \,.\, C_2H_5 \\ O \,.\, C_2H_5 \end{matrix}\right. = C_2O_2\left\langle\begin{matrix} O \,.\, C_2H_5 \\ N(CH_3)_2 \end{matrix}\right. + C_2H_5 \,.\, OH.$$

Dimethyl-oxamic Ester.

When the reaction-product is distilled, the unaltered trimethylamine passes over. Water will extract the dimethyl oxamide from the residue; on distillation with caustic potash it becomes *methylamine* and potassium oxalate:

$$C_2O_2<\begin{matrix}NH.CH_3\\NH.CH_3\end{matrix} + 2KOH = C_2O_4K_2 + 2NH_2(CH_3).$$

The insoluble dimethyl-oxamic ester is converted, by distillation with potash, into *dimethylamine*:

$$C_2O_2<\begin{matrix}O.C_2H_5\\N(CH_3)_2\end{matrix} + 2KOH = C_2O_4K_2 + NH(CH_3)_2 + C_2H_5.OH.$$

The behavior of the primary and secondary amines toward formaldehyde allows of their separation from one another (B. **29**, R. 590).

(2 *a*) The secondary aliphatic amines, *e.g.*, diethylamine (also piperidine), are readily transposed by a series of reactive non-metallic chlorides, non-metallic oxy- and sulpho-chlorides, as well as chlorides of inorganic acids. The dialkylamine residue replaces one or all of the chlorine atoms. The products are dialkylized acid amides (B. **29**, 710).

Thionyl chloride replaces both the hydrogen atoms in primary amines by the thionyl residue, with the production of *thionylamines*, the alkylized imides of sulphurous acid (Michaelis), which bear the same relation to sulphur dioxide that the isocyanic esters sustain to carbon dioxide.

The following arrangement, taking diethylamine as example, affords a review of these reactions:

$\begin{matrix}SCl\\\dot{S}Cl\end{matrix}$	$\longrightarrow$	$\begin{matrix}S—N(C_2H_5)_2\\\dot{S}—N(C_2H_5)_2\end{matrix}$	Dithio-diethylamine.
SCl_2	$\longrightarrow$	$S<\begin{matrix}N(C_2H_5)_2\\N(C_2H_5)_2\end{matrix}$	Monothio-diethylamine.
$SOCl_2$	$\nearrow$	$SON(C_2H_5)$	Thionyl-ethylamine.
	$\searrow$	$SO<\begin{matrix}N(C_2H_5)_2\\N(C_2H_5)_2\end{matrix}$	Thionyl-diethylamine.
SO_2Cl_2	$\longrightarrow$	$SO_2<\begin{matrix}N(C_2H_5)_2\\N(C_2H_5)_2\end{matrix}$	Sulphuryl- or Sulpho-diethyl-amine.
PCl_3	$\longrightarrow$	$PCl_2N(C_2H_5)_2$	Diethylamine-chlorphosphine.
$POCl_3$	$\nearrow$	$POCl_2N(C_2H_5)_2$	Diethylamine-oxychlorphosphine.
	$\searrow$	$PO[N(C_2H_5)_2]_3$	Tridiethylamine-phosphine-oxide.
$PSCl_3$	$\longrightarrow$	$PSCl_2N(C_2H_5)_2$	Diethylamine-sulphochlorphosphine.
BCl_3	$\longrightarrow$	$BCl_2N(C_2H_5)_2$	Diethylamine-chlorboride.
$SiCl_4$	$\longrightarrow$	$SiCl_3N(C_2H_5)_2$	Diethylamine-chlorsilicide.

(2 *b*) Primary and secondary amines are transposed like ammonia by organic acid chlorides—*e.g.*, acetyl chloride—into mono- and dialkyl acid amides.

(2 *c*) The primary and secondary amines deport themselves similarly with 2, 4-dinitrobrombenzene and picryl chloride or 2, 4, 6-trinitrochlorbenzene (B. **18**, R. 540).

(3) Primary and secondary amines combine with many inorganic and organic acid anhydrides—*e. g.*, sulphur trioxide, acetic anhydride—to form amic acids, and are then transposed into acid amides.

(4) The deportment of the amines toward nitrous acid is very characteristic. Primary amines are changed, at least in part, by this acid into their corresponding alcohols (p. 113):

$$C_2H_5NH_2 + NO.OH = C_2H_5OH + N_2 + H_2O.$$

This reaction corresponds to the decomposition of ammonium nitrite into water and nitrogen:

$$NH_3 + NO.OH = H_2O + N_2 + H_2O.$$

Frequently, instead of the expected secondary alcohols, those of the tertiary class are produced (B. **24**, 3350).

Nitrous acid converts the secondary amines into *nitroso-amines* (p. 170):

$$(CH_3)_2NH + NO.OH = \underset{\text{Nitroso-dimethylamine.}}{(CH_3)_2N.NO} + H_2O;$$

whereas the tertiary amines remain unaltered or undergo decompositions. Indeed, these reactions may be utilized in the separation of the amines, when naturally the primary amines are lost.

(5) Another procedure, furnishing a partial separation of the amines, depends on their varying behavior toward carbon disulphide. The free bases (in aqueous, alcoholic, or ethereal solution) are digested with CS_2, when the primary and secondary amines form salts of alkyl dithio-carbaminic acid (see this), while the tertiary amines remain unaffected, and may be distilled off. On boiling the residue with $HgCl_2$ or $FeCl_3$, a part of the primary amine is expelled from the compound as mustard oil (A. W. Hofmann, B. **8**, 105, 461; **14**, 2754; and **15**, 1290).

(6) A marked characteristic of the primary amines is their ability to form *carbylamines* (see these), which are easily recognized by their odor (A. W. Hofmann, B. **3**, 767).

(7) By the action of Cl, Br, or I alone or in the presence of caustic alkali, primary and secondary amines yield alkylamine halides (p. 169).

(8) The amines, when heated with potassium permanganate, are gradually oxidized to the corresponding aldehydes and acids, with the splitting-off of ammonia (B. **8**, 1237).

(*a*) Amines and Ammonium Bases with Saturated Alcohol Radicals.

(1) **Primary Amines.—Methylamine,** $CH_3.NH_2$, occurs in *Mercurialis perennis* and *annua*, in bone-oil, and in the distillate from wood. It is produced from the methyl ester of isocyanic acid, by the reduction of chloropicrin, $CCl_3(NO_2)$, and hydrogen cyanide, and by the decomposition of various natural alkaloids, like *theïne*, *creatine*, and *morphine*. The best way of preparing it is to warm bromacetamide with caustic potash (see p. 163).

Methylamine is a colorless gas, with an ammoniacal odor; it condenses in the cold to a liquid boiling at —6°. Its combustibility in the air distinguishes it from ammonia. At 12° one volume of water dissolves 1150 volumes of the gas. The aqueous solution manifests all the properties of aqueous ammonia, but does not, however, dissolve the oxides of cobalt, nickel, and cadmium.

Methyl ammonium chloride melts at 210°. *Methyl ammonium picrate* dissolves with difficulty, and melts at 207°.

Ethylamine, $C_2H_5 . NH_2$, is a mobile liquid, which boils at 18° and has a sp. gr. of 0.696 at 8°. It mixes with water in all proportions. It expels ammonia from ammoniacal salts, and when in excess redissolves aluminium hydroxide; otherwise it deports itself in every respect like ammonia.

Propylamine, $C_3H_7 . NH_2$, boils at 49°; **isopropylamine,** $C_3H_7 . NH_2$, obtained from dimethyl acetoxime, $(CH_3)_2C : N . OH$ (see p. 161), boils at 32° (B. **20**, 505).

The higher alkylamines with an odd number of carbon atoms are most easily obtained from the nitriles of the fatty acids, $C_nH_{2n+1}CN$ (p. 162, B. **22**, 812). The alkylamines with an even number of carbon atoms are prepared from the acid amides (p. 163, B. **21**, 2486).

Butylamine, $C_4H_9 . NH_2$ (normal), boils at 76°; **isobutylamine,** $C_4H_9 . NH_2$, obtained from fermentation butyl alcohol, boils at 68°.

Tertiary Butylamine, Trimethyl Carbinamine, boils at 43°.

Normal Amylamine, $C_5H_{11} . NH_2$, boils at 103°.

Isoamylamine, $C_5H_{11} . NH_2$, is a liquid boiling at 95°; it is obtained from leucine by distillation with caustic potash. It is miscible with water, and burns with a luminous flame.

Diethyl carbinamine, $(C_2H_5)_2CH . NH_2$, boils at 90°.

Di-n-**propyl carbinamine** $(C_3H_7)_2CHNH_2$, boils at 130°; **di-iso-butyl carbinamine,** $(C_4H_7)_2CHNH_2$, melts at 166°. All these are obtained from the corresponding ketoximes by reduction with sodium and alcohol (B. **27**, R. 200).

n-**Nonylamine,** $C_9H_{19} . NH_2$, boils at about 195°, and is sparingly soluble in water.

(2) **Secondary Amines.**—The secondary amines are also designated *imide bases. Simple Secondary Amines:*

Dimethylamine, $NH(CH_3)_2$, is most conveniently obtained by boiling nitroso-dimethyl aniline or dinitro-dimethyl aniline with caustic potash (A. **222**, 119). It is a gas that dissolves readily in water. It is condensed to a liquid by cold, and boils at 7.2°.

Diethylamine, $NH(C_2H_5)_2$, is a liquid boiling at 56°, and is readily soluble in water. Its HCl-salt fuses at 176° and its picrate at 155° (B. **29**, R. 590).

Di-n-propylamine boils at 110°. *Di-isopropylamine* boils at 84° (B. **22**, R. 343). Mixed secondary amines are produced by methods 3*a* and 3*b*. *Methyl-ethylamine* boils at 35°. *Methyl-n-propylamine* boils at 63°. *Methyl-n-butylamine* boils at 91°. *Methyl-n-heptylamine* boils at 171° (B. **29**, 2110).

(3) **Tertiary Amines.**—These are also called *nitrile* bases, to distinguish them from *alkyl cyanides* or *acid nitriles.*

Trimethylamine, $N(CH_3)_3$. This is isomeric with *ethyl-methylamine*, $C_2H_5 . NH . CH_3$, and the two propylamines, $C_3H_7 . NH_2$. It is present in herring-brine, and is produced by distilling betaïne (from the beet) with caustic potash. It is prepared from herring-brine in large quantities, and also by the distillation of the "vinasses" of the French beet root. Trimethylamine is a liquid, very soluble in water, and boils at 3.5°. The penetrating, fish-like smell is characteristic of it. Its HCl-salt melts at 271–275°, and its sparingly soluble picrate at 216° (B. **29**, R. 590).

Triethylamine, $N(C_2H_5)_3$, boils at 89°, and is not very soluble in water. It is produced by heating ethyl isocyanate with sodium ethylate: $CO:N.C_2H_5 + 2C_2H_5.ONa = N(C_2H_5)_3 + CO_3Na_2$.

(4) **Tetraalkyl Ammonium Bases.**—While neither ammonium hydroxide nor mono-, di-, or tri-alkyl ammonium hydroxides have been prepared, yet, by the addition of the alkyl iodides to the tertiary amines, tetraalkyl ammonium iodides are produced; when treated with moist silver oxide they yield the *ammonium hydroxides:*

$$N(C_2H_5)_4I + AgOH = N(C_2H_5)_4.OH + AgI.$$

These hydroxides are perfectly analogous to those of potassium and sodium. They possess strong alkaline reaction, saponify fats, and deliquesce in the air. They crystallize when their aqueous solutions are concentrated in vacuo. With the acids they yield ammonium salts; these usually crystallize well.

On exposure to strong heat they break down into tertiary amines and alcohols, or their decomposition products (C_nH_{2n} and H_2O):

$$N(C_2H_5)_4.OH = N(C_2H_5)_3 + C_2H_4 + H_2O.$$

This reaction has acquired special significance because of its application in the decomposition of ring-shaped bases (see piperidine or pentamethylene imide).

Tetramethyl Ammonium Iodide or *Tetramethylium Iodide*, $N(CH_3)_4I$, and *Tetraethyl Ammonium Iodide* or *Tetraethylium Iodide*, $N(C_2H_5)_4I$, from trimethylamine (triethylamine) and ethyl iodide, consist of white prisms crystallized from water or alcohol.

Tetramethylium Hydroxide, $N(CH_3)_4OH$, and *Tetraethylium Hydroxide*, $N(C_2H_5)_4OH$, consist of deliquescent needles with a strong alkaline reaction. They result when the corresponding iodides are treated with moist silver oxide.

Iodine Addition Products.—$(C_2H_5)_4NI.I_2$, $(C_2H_5)_4NI.2I_2$, and addition products containing even more iodine molecules, are precipitated by iodine from the aqueous solutions of the tetraalkylium iodides, *e. g.*, tetraethylium iodide.

Of the numerous compounds belonging here we may mention:

Dimethyl-diethyl Ammonium Iodide, $\left.\begin{matrix}(CH_3)_2\\(C_2H_5)_2\end{matrix}\right\}NI$, obtained from dimethylamine and ethyl iodide, and from diethylamine and methyl iodide:

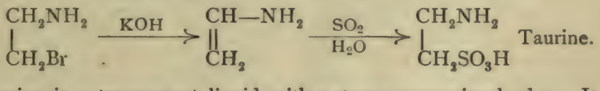
$$\left.\begin{matrix}CH_3\\CH_3\\C_2H_5\end{matrix}\right\}N.C_2H_5I \quad \text{and} \quad \left.\begin{matrix}C_2H_5\\C_2H_5\\CH_3\end{matrix}\right\}N.CH_3I.$$

These two compounds are identical (A. **180**, 173). They demonstrate, too, that the ammonium compounds are not molecular derivatives, as formerly assumed (the above formulas are only intended to exhibit the different manner of formation), but represent true atomic compounds. They further show the equivalence of the five nitrogen valences (compare Le Bel, B. **23**, R. 147).

For the dissymmetry and the appearance of rotatory power in alkyl derivatives of ammonium chloride, compare Le Bel, B. **24**, R. 441, who succeeded, by use of germ vegetation, in changing isobutyl-propyl-ethyl-methyl-ammonium chloride into an optically active modification.

(*b*) Unsaturated Amines and Ammonium Bases.

Vinylamine, $CH_2 = CH . NH_2$, boiling at 55°, is only known in solution. It results from the action of silver oxide or potassium hydroxide upon brom-ethylamine (see this). It unites with sulphur dioxide to form *Taurine* (see this):



$$\begin{array}{l} CH_2NH_2 \\ | \\ CH_2Br \end{array} \xrightarrow{KOH} \begin{array}{l} CH-NH_2 \\ \| \\ CH_2 \end{array} \xrightarrow[H_2O]{SO_2} \begin{array}{l} CH_2NH_2 \\ | \\ CH_2SO_3H \end{array} \text{ Taurine.}$$

Vinylamine is a transparent liquid with a strong ammoniacal odor. It corrodes the skin, and is soluble in water. *Vinyl Picrate* melts at 142° (B. **28**, 2929).

Trimethyl-vinyl Ammonium Hydroxide or *Neurine*, $CH_2 = CH . N(CH_3)_3OH$, is described after glycol with choline, to which it is intimately related.

Allylamine, $CH_2 = CH . CH_2 . NH_2$, from mustard oil (see this), boils at 58°.

Isoallylamine, Propenylamine, $CH_3 . CH = CHNH_2$, boils at 67°. It is produced by the action of caustic potash on β-brompropylamine (B. **29**, 2747).

Dimethyl Piperidine, *Pentallyl Dimethylamine*, $CH_2 = CH . CH_2 . CH_2 . CH_2 . N(CH_3)_2$. It is a decomposition product of piperidine (see this). It boils at 117–118°. This and similar bases take up hydrochloric acid, and when heated yield ammonium chlorides of pyrrolidine bases (A. **278**, 1).

Propargylamine, $CH \equiv C . CH_2NH_2$, from dibromallylamine, $CH_2Br . CHBr . CH_2NH_2$, and alcoholic potash, is probably a gas in a free condition. It could only be obtained in alcoholic solution or in the form of salts (B. **22**, 3080).

(*c*) Alkylamine Halides.

These bear the same relation to NCl_3 and NI_3 as the alkylamines sustain to ammonia. The alkylamine chlorides and bromides may also be regarded as the amides of hypochlorous and hypobromous acids. Such derivatives are produced by the action of chlorine, bromine, or iodine alone, or in the presence of caustic alkalies, upon primary and secondary amines (B. **8**, 1470; **9**, 146; **16**, 558; **23**, R. 386; A. **230**, 222), as well as by the transposition of *acetdibromamide* (see this) with amines. When saponified they yield hypochlorous, hypobromous, and hypoiodous acids (B. **26**, 985):

$$CH_3.CH_2.CH_2NH_2 \longrightarrow CH_3.CH_2.CH_2NHCl \longrightarrow CH_3.CH_2.CH_2.NCl_2$$
$$(CH_3.CH_2CH_2)_2NH \longrightarrow (CH_3CH_2CH_2)_2NCl.$$

The primary alkylamine mono-halides are more unstable than the dihalides and the secondary halogen-amines.

Methylamine Diiodide, CH_3NI_2, is garnet-red in color. *Dimethylamine Iodide*, $(CH_3)_2NI$, is sulphur-yellow in color. *Ethylamine Dichloride* is an unstable oil, with penetrating odor, and boils at 88–89°. *Propylamine Chloride*, C_3H_7NHCl, volatilizes with decomposition. *Propylamine Dichloride*, $C_3H_7NCl_2$, is a yellow oil, boiling at 117°. *Dipropylamine Chloride*, $(C_3H_7)_2NCl$, boils at 143° (B. **8**, 1470; **9**, 146; **16**, 558; **23**, R. 386; **26**, R. 188; A. **230**, 222).

Nitriles result when the dibromides of the higher primary alkylamines are treated with alkalies.

(*d*) Sulphur-containing Derivatives of the Alkylamines.

1. *Thiodialkylamines*, Thiotetralkyldiamines, result from the action of SCl_2 upon dialkylamines in ligroïne solution. *Thiodiethylamine*, $S[N(C_2H_5)_2]_2$, boils at 87° (19 mm.) (B. **28**, 575).

2. *Dithiotetralkylamines*, Dithiotetralkyldiamines, result from the action of S_2Cl_2 upon dialkylamines in ethereal solution. *Dithiodimethylamine*, $S_2[N(CH_3)_2]_2$, boils at 82° (22 mm.). *Dithiodiethylamine* boils at 137° (29 mm.) (B. **28**, 166).

3. *Alkyl-thionylamines*, alkylized imides of sulphurous acid, are formed when thionyl chloride (1 mol.) acts upon a primary amine (3 mols.) in ethereal solution (Michaelis A. **274**, 187):

$$3CH_3NH_2 + SOCl_2 = CH_3N = SO + 2CH_3NH_2 . HCl.$$

The members of the series with low boiling points are liquids with penetrating odor, and fume in the air. Water decomposes them into SO_2 and the primary amine. *Thionyl-methylamine*, CH_3NSO, boils at 58–59°. *Thionyl-ethylamine* boils at 70–75°. *Thionyl-isobutylamine*, $(CH_3)_2CH . CH_2 . N : SO$, boils at 117°.

4. **Thionyl Dialkylamines,** Thionyl Tetralkyldiamines, are formed when thionyl chloride acts upon the ethereal solution of the dialkylamines. *Thionyl Diethylamine*, $OS[N(C_2H_5)_2]_2$, boiling at 118° (27 mm.), corresponds in its composition to tetraethyl urea (B. **28**, 1016).

5. **Thionamic Acids** are the products resulting from the interaction of sulphur dioxide and primary amines: $C_2H_5NH . SO_2H$, *ethyl thionamic acid*, a white hygroscopic powder.

6. **Alkyl Sulphamides** and **Alkyl Sulphaminic Acids.** Sulphamides, *e. g.*, $SO_2<^{N(CH_3)_2}_{N(CH_3)_2}$, are formed by the action of sulphuryl chloride, SO_2Cl_2, upon the free secondary amines, whereas their chlorides, $SO_2<^{NR_2}_{Cl}$ result when the HCl-salts are employed. Water converts the chlorides into sulphaminic acids, $SO_2<^{NR_2}_{OH}$ (A. **222**, 118). SO_3 reacts similarly with the primary and secondary amines, forming mono- and dialkyl-sulphaminic acids (B. **16**, 1265).

(*e*) Nitroso-amines.

All basic secondary amines (imides), like $(CH_3)_2NH$ and $(C_2H_5)_2NH$, can become nitroso-amines through the replacement of the hydrogen of the imide group. They are obtained from the free imides by the action of nitrous acid upon their aqueous, ethereal, or glacial acetic acid solutions, or by warming their salts in aqueous or acid solution with potassium nitrite (B. **9**, 111). They are mostly oily, yellow liquids, insoluble in water, and may be distilled without suffering decomposition. Alkalies and acids are usually without effect upon them; with phenol and sulphuric acid they give the nitroso-reaction. When reduced in alcoholic solution by means of zinc dust and acetic acid they become hydrazines (p. 161). Boiling hydrochloric acid decomposes them into nitrous acid, and dialkylamines.

Dimethyl Nitrosamine, Nitrosodimethylin, $(CH_3)_2N . NO$, boils at 148°.

Diethyl Nitrosamine, $(C_2H_5)_2N . NO$, Nitrosodiethylin, boils at 177°.

(*f*) Nitramines

are produced by the action of concentrated nitric acid upon various amide derivatives of the primary amines, *e. g.*, their urethanes, from which the free monoalkyl nitramines may be obtained by splitting off ammonia (B. **18**, R. 146; **22**, R. 295):

$$CH_3NHCO_2CH_3 \longrightarrow CH_3N(NO_2)CO_2CH_3 \longrightarrow CH_3 . NH . NO_2.$$

The imide hydrogen atom of the monoalkyl nitramines can be replaced by metals. Simple and mixed dialkyl nitramines result from the transposition of the potassium alkyl nitroamine derivatives with alkylogens. By reduction of the dialkyl nitramines with zinc dust and acetic acid, unsymmetrical dialkyl hydrazines are produced.

Methyl-nitramine, $CH_3 . NH(NO_2)$, melts at 38°. **Ethyl-nitramine,** $C_2H_5 . NH(NO_2)$, melts at 3°. **Propyl-nitramine** boils at 128° (40 mm.). **Butyl-nitramine,** see B. **28**, R. 1058.

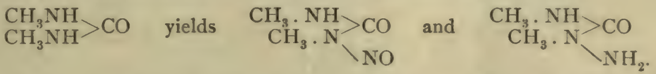
Simple Dialkyl-nitramines: Dimethyl-nitramine, $(CH_3)_2N . NO_2$, melts at 58°, boils at 187°, and is produced, together with an isomeride, boiling at 112°, by the distillation of mono-methyl-nitramine (B. **29**, R. 910), as well as upon treating dimethylamine and nitric acid with acetic anhydride (B. **28**, 402). *Diethyl-nitramine* boils at 206°. *Dipropyl-nitramine* boils at 77° (10 mm.). *Mixed Nitramines: Methyl-ethyl-nitramine* boils at 190°. *Methyl-propyl-nitramine* boils at 115° (40 mm.). *Methyl-butyl-nitramine* melts at + 0.5° (B. **29**, R. 424). *Methyl-allyl-nitramine*, boiling at 95° (18 mm.), is obtained, together with an isomeride, boiling at 51° (18 mm.), by the interaction of potassium methyl-nitramine and allyl bromide.

(*g*) Alkyl-hydrazines.

Just as the *amines* are derived from ammonia, NH_3, so the hydrazines are derived from *hydrazine* or *diamide*, $H_2N—NH_2$, an analogue of liquid hydrogen phosphide, $H_2P—PH_2$.

Long before hydrazine in a free state was obtained from diazo-acetic acid (see this), its derivatives had been prepared by a variety of methods. They hold an important place in the benzene series (see phenylhydrazine, $C_6H_5 . NH . NH_2$) (E. Fischer, A. **99**, 281).

The *mono-alkyl hydrazines* are obtained from the mono-alkyl ureas, $NH_2 . CO . NH . R$, and from the symmetrical dialkylureas by their conversion into nitroso-compounds, and the reduction of the latter to hydrazines of the ureas:



$$\left.\begin{matrix}CH_3NH\\CH_3NH\end{matrix}\right>CO \quad \text{yields} \quad \left.\begin{matrix}CH_3 . NH\\CH_3 . N\end{matrix}\right>CO \atop \quad\searrow NO \quad \text{and} \quad \left.\begin{matrix}CH_3 . NH\\CH_3 . N\end{matrix}\right>CO \atop \quad\searrow NH_2.$$

When the latter are heated with alkalies or acids they split up, like all urea derivatives, into their components, CO_2, alkylamine and alkylhydrazine. They reduce Fehling's solution in the cold, while heat is necessary to effect this when using the dialkyl hydrazines. In this respect they differ from the amines, which they so closely resemble in properties.

Methyl Hydrazine, $CH_3 . NH . NH_2$, is a very mobile liquid, boiling at 87°. Its odor is like that of methylamine. In the air it absorbs moisture and fumes (B. **22**, R. 670).

Ethyl Hydrazine, $(C_2H_5)HN . NH_2$, boils at 100°.

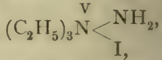
When ethyl hydrazine is acted upon by potassium disulphate, *potassium ethyl hydrazine sulphonate*, $C_2H_5 . NH — NH . SO_3K$, is formed. Mercuric oxide changes this to *potassium diazo-ethyl sulphonate*, $C_2H_5 . N = N . SO_3K$. This is the only well-known representative in the fatty-series of a numerous and highly important class of derivatives of the benzene series—the *diazo-compounds*. They are characterized by the *diazo group*, —N=N—, which is in union with carbon radicals.

s-*Dialkyl hydrazines* result, through the action of hydrochloric acid, from the corresponding diformyl compounds, which are the reaction products of alkyl iodides and lead diformyl-hydrazine. s-*Diethyl hydrazine*, $C_2H_5NH—NH . C_2H_5$, boils at 85° (B. **27**, 2279).

The uns-**Dialkylhydrazines,** like $(CH_3)_2N . NH_2$, are formed by the reduction of nitroso-amines and dialkyl nitramines (B. **29**, R. 424), in aqueous and alcoholic solution, by zinc dust and acetic acid:

$$(CH_3)_2N . NO + 2H_2 = (CH_3)_2N . NH_2 + H_2O.$$

uns-**Dimethyl Hydrazine,** $(CH_3)_2N.NH_2$, and uns-**Diethyl Hydrazine.** $(C_2H_5)_2N . NH_2$, are mobile liquids, of ammoniacal odor, and readily soluble in water, alcohol, and ether. Diethyl hydrazine boils at 97°, and the dimethyl compound at 62°. *Thionyl Diethylhydrazine*, $(C_2H_5)_2N.NSO$, boils at 73° under 20 mm. (B. **26**, 310).

Diethylhydrazine unites with ethyl iodide and yields the compound $(C_2H_5)_2.N.NH_2.C_2H_5I$, which is to be viewed as the *ammonium iodide*,  $(C_2H_5)_3\overset{V}{N}\!<^{NH_2}_{I}$, as it is not decomposed by alkalies, and moist silver oxide converts it into a strong alkaline hydroxide. Nascent hydrogen (zinc and sulphuric acid) decomposes this iodide into triethylamine, ammonia, and hydrogen iodide.

This reaction is an additional proof that the ammonium compounds represent atomic derivatives of quinquivalent nitrogen (A. **199**, 318).

(*h*) Tetra-alkyl-tetrazones.

When mercuric oxide acts upon diethylhydrazine, *tetraethyl-tetrazone*, $(C_2H_5)_2N.N:N.N(C_2H_5)_2$, is formed. This is a strong basic liquid with an alliaceous odor.

Methyl-butyl-tetrazone boils at 121° (19 mm.) (B. **29**, R. 424).

(*i*) Alkyl Hydroxylamine Derivatives.

The entrance of one alkyl group into hydroxylamine produces two isomeric forms:

$NH_2.O.CH_3$	and	$CH_3.NH.OH.$
α-Methyl-hydroxylamine.		β-Methyl-hydroxylamine.

The derivatives of both varieties are obtained from the isomeric benzaldoximes (see these). The β-compounds are formed from syn-meta-nitrobenzaldoxime by alkylization with sodium alcoholate and an alkyl iodide, together with the subsequent splitting-off of the ether by means of concentrated hydrochloric acid (B. **23**, 599; **26**, 2377, 2514). α-Derivatives result from the breaking down of alkyl benzhydroxamic esters, and the β-bodies are intermediate products in the reduction of the nitroparaffins with stannous chloride, or, better, with zinc dust and water (B. **27**, 1350).

α-Methylhydroxylamine, $NH_2.O.CH_3$, *Methoxylamine*, yields an HCl-salt, which melts at 149°. It differs from hydroxylamine in that it does not reduce alkaline copper solutions.

α-Ethylhydroxylamine, $NH_2.O.C_2H_5$, *Ethoxylamine*, boils at 68°.

β-Methylhydroxylamine, $CH_3.NH.OH$, melts at 41–42°, and boils at 61–62° (16 mm.) (B. **23**, 3597; **24**, 3528; **25**, 1716; **26**, 2514).

β-Ethylhydroxylamine melts at 59–60°.

The action of ethyl bromide upon ethoxylamine produces *Diethylhydroxylamine*, $C_2H_5.NH.O.C_2H_5$, and *Triethylhydroxylamine*, $(C_2H_5)_2.N.O.C_2H_5$, boiling at 98° (B. **22**, R. 590). *Triethylamine Oxide*, $(C_2H_5)_3N:O$, an isomeride of the latter, has been prepared by the interaction of zinc ethide and nitroethane. It boils at 155° (B. **22**, R. 250).

(*k*) Phosphorus Derivatives of Secondary Alkylamines (B. **29**, 710).

1. *Dialkylamine Chlorphosphines* are formed when phosphorus trichloride acts upon dialkylamines. They are liquids having a sharp, penetrating odor; they fume in the air. *Diethylamine Chlorphosphine*, $(C_2H_5)_2N.PCl_2$, boils at 100° (14 mm.). *Di-isobutylamine Chlorphosphine* melts at 37° and boils at 116° (16 mm.).

2. *Dialkylamine Oxychlorphosphines.*—These result when phosphorus oxychloride acts upon secondary amines in ethereal solution. They are stable in the air, and possess an aromatic odor resembling that of camphor or pepper. *Dialkylamine Oxychlorphosphine*, $(C_2H_5)_2N.POCl_2$, boils at 100° (15 mm.). *Di-n-propylamine Oxychlorphosphine* boils at 170° (80 mm.). *Di-isobutylamine Oxychlorphosphine* melts at 54°.

3. *Dialkylamine Sulphochlorphosphines* result from the interaction of phosphorus sulphochloride and the dialkylamines. They are volatile in steam. Their odor is like that of camphor.

Diethylamine Sulphochlorphosphine, $(C_2H_5)_2NPSCl_2$, boils at 100° (15 mm.). *Dipropylamine Sulphochlorphosphine* boils at 133° (15 mm.). *Di-isobutylamine Sulphochlorphosphine* boils at 150° (10 mm.).

(*l*) (*m*) (*n*) Arsenic, Boron, and Silicon Derivatives of Secondary Amines (B. 29, 714).

(*l*) *Di-isobutylamine Chlorarsine*, $(C_4H_9)_2N . AsCl_2$, boils at 125° (15 mm.).

(*m*) *Diethylamine Chlorborine*, $(C_2H_5)_2N . BCl_2$, boils at 142°, and fumes very strongly in the air. *Dipropylamine Chlorborine* boils at 99° (45 mm.). *Di-isobutylamine Chlorborine* boils at 93° (17 mm.).

(*n*) *Diethylamine Chlorsilicide*, $(C_2H_5)_2N . SiCl_3$, boils at 104° (80 mm.). *Di-isobutylamine Chlorsilicide* boils at 122° (30 mm.). The chlorarsines, chlorborines, and chlorsilicides are prepared from their corresponding chlorides.

6. PHOSPHORUS DERIVATIVES OF THE ALCOHOL RADICALS.

A. PHOSPHORUS BASES OR PHOSPHINES AND ALKYL PHOSPHONIUM COMPOUNDS.

Hydrogen phosphide, PH_3, has slight basic properties. It unites with HI to phosphonium iodide, which is resolved again by water into its components. The *phosphorus bases or phosphines*, obtained by the replacement of the hydrogen of PH_3 by alkyls, have more of the basic character of ammonia and approach the amines in this respect. The basic character increases with the number of alkyl groups.

(1) They oxidize very energetically on exposure to the air, usually with spontaneous ignition; hence they should be prepared away from air contact. Moderate oxidation with nitric acid converts the primary phosphines into *alkyl phosphoric acids*, the secondary phosphines into *alkyl phosphinic acids*, while the tertiary phosphines, in the presence of air, pass into *alkyl phosphinic oxides :*

Ethyl Phosphine: $C_2H_5PH_2 \longrightarrow C_2H_5PO(OH)_2$—Ethyl Phosphoric Acid
Diethyl Phosphine: $(C_2H_5)_2PH \longrightarrow (C_2H_5)_2PO(OH)$—Diethyl Phosphinic Acid
Triethyl Phosphine: $(C_2H_5)_3P \longrightarrow (C_2H_5)_3PO$—Triethyl Phosphine Oxide.

(2) They combine readily with sulphur and carbon disulphide (B. 25, 2436); also with the halogens.

(3) The primary phosphines, *e. g.*, PH_3, are feeble bases. Their salts, like PH_4I, are decomposed by water. Caustic potash is required for the decomposition of the salts of the secondary and tertiary phosphines.

(4) The tertiary phosphines combine with the alkyl iodides to form tetra-alkyl phosphonium iodides. These are just as little decomposed by caustic potash as the tetra-alkyl ammonium iodides. Moist silver oxide liberates *tetra-alkyl phosphonium hydroxides* from them ; these, like the tetra-alkyl ammonium hydroxides, are stronger bases than the alkalies :

$$P(CH_3)_3 \xrightarrow{CH_3I} P(CH_3)_4I \xrightarrow{Ag(OH)} P(CH_3)_4OH.$$

Thénard (1846) discovered the tertiary phosphines, and A. W. Hofmann (1871) first prepared the primary and secondary phosphines (B. **4**, 430).

Formation.—(1) By letting the alkyl iodides act upon phosphonium iodide for six hours in the presence of certain metallic oxides, chiefly zinc oxide, at 150°. The product is a mixture of $P(C_2H_5)H_2 . HI$ and $P(C_2H_5)_2H . HI$, the first of which is decomposed by water. The HI-salt of the diethyl phosphine is not affected, but by boiling the latter with sodium hydroxide, diethyl phosphine is set free (A. W. Hofmann):

$$2PH_4I + 2C_2H_5I + ZnO = 2[P(C_2H_5)H_2 . HI] + ZnI_2 + H_2O$$
$$PH_4I + 2C_2H_5I + ZnO = P(C_2H_5)_2H . HI \quad + ZnI_2 + H_2O.$$
$$P(C_2H_5)H_2HI \xrightarrow{H_2O} P(C_2H_5)H_2 + HI.$$

(2) Tertiary phosphines and phosphonium iodides are produced by heating phosphonium iodide with alkyl iodides (methyl iodide) to 150°–180° without the addition of metallic oxides. They can be separated by means of caustic potash:

$$PH_4I + 3CH_3I = P(CH_3)_3 . HI + 3HI$$
$$P(CH_3)_3HI + CH_3I = P(CH_3)_4 . I + HI.$$

(3) Tertiary phosphines result when alkylogens act upon calcium phosphide (Thénard), and (4) in the action of zinc alkyls upon phosphorous chloride:

$$2PCl_3 + 3Zn(CH_3)_2 = 2P(CH_3)_3 + 3ZnCl_2.$$

The *phosphines* are colorless, strongly refracting, extremely powerful-smelling, volatile liquids. They are scarcely soluble in water, but dissolve readily in alcohol and ether. They oxidize very readily and show neutral reaction.

(1) **Primary Phosphines:**

Methyl Phosphine, $P(CH_3)H_2$, condenses at —14° to a mobile liquid.

Ethyl Phosphine, $P(C_2H_5)H_2$, boils at 25°.

Isopropyl Phosphine, $P(C_3H_7)H_2$, boils at 41°, and the **isobutyl** derivative, $P(C_4H_7)H_2$, at 62°. Fuming nitric acid oxidizes the primary phosphines to *alkyl phospho-acids;* their HI-salts are decomposed by water.

(2) **Secondary Phosphines:**

Dimethyl Phosphine, $P(CH_3)_2H$, boils at 25° C.

Diethyl Phosphine, $P(C_2H_5)_2H$, boils at 85°.

Di-isopropyl Phosphine, $P(C_3H_7)_2H$, boils at 118°. **Di-isoamyl Phosphine,** $P(C_5H_{11})_2H$, boils at 210°–215°, but is not self-inflammable. Fuming nitric acid oxidizes this class of phosphines to *dialkyl phosphinic acids.*

Water does not decompose the HI-salts of the secondary phosphines.

(3) **Tertiary Phosphines:**

Trimethyl Phosphine, $P(CH_3)_3$, boils at 40°. **Triethyl Phosphine,** $P(C_2H_5)_3$, boils at 117°. Both tertiary phosphines form phosphine oxides by the absorption of oxygen (B. **29**, 1707). They also combine with S, Cl_2, Br_2, the halogen hydrides, and the alkylogens. Carbon disulphide also combines with triethyl phosphine, and the product is $P(C_2H_5)_3 . CS_2$, crystallizing in red leaflets. It is insoluble in water, fuses at 95°, and sublimes without decomposition. Its production will answer for the detection of carbon disulphide.

According to almost all of these reactions, triethyl phosphine resembles a strongly positive bivalent metal—for example, calcium. By the addition of three alkyl groups, the quinquivalent, metalloidal phosphorus atom acquires the character of a bivalent alkaline earth metal. By the further addition of an alkyl to the phosphorus in the phosphonium group, $P(CH_3)_4$, the former acquires the properties of a univalent alkali metal. Similar conditions manifest themselves with sulphur, with tellurium, with arsenic, and also with almost all the less positive metals.

(4) *Phosphonium Bases.*—The *tetra-alkyl phosphonium bases* resemble, in a very high degree, both in formation and properties, the tetra-alkyl ammonium bases.

Tetra-methyl- and *Tetra-ethyl-phosphonium Hydroxide*, $P(C_2H_5)_4 . OH$, are crystalline masses which deliquesce on exposure to the air. They show a strong alkaline reaction. When they are heated they show the great affinity of phosphorus for oxygen, for, unlike the corresponding ammonium derivatives, they break down into a *trialkyl phosphine oxide* and a paraffin. Thus *tetra-methyl-phosphonium hydroxide* yields trimethyl phosphine oxide and methane: $P(CH_3)_4 . OH = P(CH_3)_3O + CH_4$.

Tetramethyl- and *Tetra-ethyl phosphonium iodide*, $P(C_2H_5)_4I$, are white, crystalline bodies. Heat decomposes them into trialkyl phosphines and alkyl iodides.

B. ALKYL PHOSPHO-ACIDS.

These acids result, as previously mentioned, from the moderated oxidation of the primary phosphines with nitric acid. They are derived from *unsymmetrical phosphorous acid*, $HPO(OH)_2$.

Methyl Phospho-acid, $CH_3PO(OH)_2$, melts at 105°. PCl_5 converts it into CH_3POCl_2, melting at 32° and boiling at 163°. The *ethyl phospho-acid*, $C_2H_5(OH)_2PO$. melts at 44°.

C. ALKYL PHOSPHINIC ACIDS.

These are derived from *hypophosphorous acid*, $H_2PO(OH)$. They are produced, as described, by oxidizing the *secondary phosphines* with fuming nitric acid. *Dimethyl Phosphinic Acid*, $(CH_3)_2PO(OH)$, resembles paraffin. It melts at 76° and volatilizes without decomposition. See B. **25**, 2441, for *diethyl-dithio-phosphinic acid*, $(C_2H_5)_2$-PSSH.

D. ALKYL PHOSPHINE OXIDES.

arise when the tri-alkyl phosphines are oxidized in the air, or by mercuric oxide; also in the decomposition of the *tetra-alkyl phosphonium hydroxides* by heat. *Triethyl Phosphine Oxide*, $P(C_2H_5)_3O$, melts at 53° and boils at 243°. It forms, for example, $P(C_2H_5)_3Cl_2$, with haloid acids, from which Na regenerates *triethyl phosphine* when aided by heat. The corresponding *tri-ethyl phosphine sulphide*, $P(C_2H_5)_3S$, from triethyl phosphine and sulphur, melts at 94°. Derivatives of PCl_3, corresponding to the alkyl chloramines, are known (B. **13**, 2174).

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7. ARSENIC ALKYL COMPOUNDS.

Arsenic is quite metallic in its character; its alkyl compounds constitute the transition from the nitrogen and phosphorus bases to the so-called metallo-organic derivatives—*i. e.*, the compounds of the alkyls with the metals (p. 182). The similarity to the amines and phosphines is observed in the existence of tertiary arsines, $As(CH_3)_3$, but these do not possess basic properties, nor do they unite with acids. They show in a marked degree the property of the tertiary phosphines, in their uniting with oxygen, sulphur, and the halogens to form compounds of the type $As(CH_3)_3X_2$. Mono- and dialkyl arsines are not known. Tri-alkyl derivatives exist. These are, however, not so important as the *cacodyl compounds* have been in the development of organic chemistry.

In 1760 Cadet discovered the reaction which led to the study of the arsenic alkyls. He distilled arsenious acid together with potassium acetate, and obtained a liquid which was subsequently named, after its discoverer, *Cadet's fuming, arsenical liquid.* From 1837–1843 Bunsen carried out a series of splendid investigations (A. **37**, 1; **42**, 14; **46**, 1), and demonstrated that the chief constituent of Cadet's liquid was "alkarsine," or cacodyl oxide, whose radical "cacodyl" Bunsen also succeeded in preparing. Berzelius proposed the name *cacodyl* (from *κακώδης*, *stinking*) for this very poisonous body with an extremely disgusting odor. Bunsen showed that it conducted itself like a compound radical. Together with the *cyanogen* of Gay-Lussac, and the *benzoyl* of Liebig and Wöhler, assumed to be present in the *benzoyl* derivatives, it formed a strong support for the radical theory. But later it was found that cacodyl was no more a free radical than was cyanogen, but that, in accordance with the doctrine of valence, it was rather a compound of two univalent radicals —$As(CH_3)_2$, combined to a saturated molecule: $\begin{array}{l}As(CH_3)_2\\ |\\ As(CH_3)_2.\end{array}$

Valuable contributions have been made to the chemistry of the arsenic alkyls by Cahours and Riche (A. **92**, 361), by Landolt (A. **92**, 370), and particularly by Baeyer, who discovered the monomethyl arsenic derivatives, and made clear the connection existing between the alkyl-arsenic derivatives (A. **107**, 257).

The following reactions give rise to arsenic alkyl compounds:

(1) *Cacodyl Oxide*, or *Alkarsine*, is produced by the distillation of potassium acetate and arsenious acid. This is a delicate test, both for arsenic and for acetic acid:

$$4CH_3 . CO_2K + As_2O_3 = [(CH_3)_2As]_2O + 2CO_3K_2 + 2CO_2.$$

(2) By the action of zinc alkyls upon arsenic trichloride, and (3) by the action of the alkyl iodides upon sodium arsenide:

$$\begin{aligned}2AsCl_3 + 3Zn(CH_3)_2 &= 2As(CH_3)_3 + 3ZnCl_2\\ AsNa_3 + 3C_2H_5I &= As(C_2H_5)_3 + 3NaI.\end{aligned}$$

(4) The transposition of trisodium arsenite by alkyl iodides gives rise to the sodium salts of alkyl arsonic acid (A. **249**, 147):

$$AsO_3Na_3 + CH_3I = CH_3AsO(ONa)_2 + NaI.$$

Table of the Alkyl- (Methyl-) Derivatives of Arsenic.

CH_3AsCl_2,	Methyl Arsendichloride.	CH_3AsO,	Methyl Arsenoxide.	$CH_3 . AsO(OH)_2$,	Methyl Arsonic Acid.
$(CH_3)_2AsCl$,	Cacodyl Chloride.	$[(CH_3)_2As]_2O$,	**Cacodyl Oxide.**	$(CH_3)_2AsO.OH$,	Cacodylic Acid.
$(CH_3)_3As$,	Trimethyl Arsine.	$(CH_3)_3AsO$,	Trimethyl Arsine Oxide.		
$(CH_3)_4AsI$,	Tetramethyl Arsonium Iodide.	$(CH_3)_4AsOH$,	Tetramethyl Arsonium Hydroxide.		
$\begin{array}{l}(CH_3)_2—As\\ \quad\quad\;\; |\\ (CH_3)_2—As\end{array}$	**, Cacodyl.**				

MONO-ALKYL ARSINE COMPOUNDS.

The formation of monomethyl arsenic chloride, $As(CH_3)Cl_2$, is due to the property, possessed by the derivatives of the type AsX_3, of adding two halogen atoms (Cl_2) and passing into compounds of the form AsX_5. The more chlorine atoms these bodies contain, the more readily do they split off methyl chloride. Thus $As(CH_3)Cl_4$ breaks down, at 0°, into $AsCl_3$ and CH_3Cl, and $As(CH_3)_2Cl_3$, at 50°, into $As(CH_3)Cl_2$ and CH_3Cl:

$$\begin{array}{lllll} As(CH_3)_3 & \xrightarrow{+Cl_2} & As(CH_3)_3Cl_2 & \xrightarrow{\qquad} & CH_3Cl + As(CH_3)_2Cl \\ As(CH_3)_2Cl & \xrightarrow{+Cl_2} & As(CH_3)_2Cl_3 & \xrightarrow{50^\circ} & CH_3Cl + As(CH_3)Cl_2 \\ As(CH_3)Cl_2 & \xrightarrow{+Cl_2} & As(CH_3)\,Cl_4 & \xrightarrow{0^\circ} & CH_3Cl + AsCl_3. \end{array}$$

Methylarsen-dichloride, $As(CH_3)Cl_2$, results in the decomposition of cacodylic acid, and of $As(CH_3)_2Cl_3$, with hydrochloric acid:

$$As(CH_3)_2O\,.\,OH + 3HCl = As(CH_3)Cl_2 + CH_3Cl + 2H_2O.$$

It is a heavy liquid, soluble in water, and boils at 133°. At —10° it unites with chlorine, forming $As(CH_3)Cl_4$. From the alcoholic solution hydrogen sulphide precipitates the *sulphide*, $As(CH_3)S$, melting at 110°.

When sodium carbonate acts upon the aqueous solution of the dichloride *methylarsenoxide*, $As(CH_3)O$, is formed. It melts at 95°, and distils along with steam. The oxide is basic, and may be converted by the haloid acids and H_2S into the halogen derivatives, $AsCH_3X_2$, and the sulphide, $AsCH_3S$.

Silver oxide, acting upon the aqueous solution of the above oxide, changes it into the silver salt of monomethyl arsonic acid, $(CH_3)AsO(OH)_2$, an analogue of methyl phospho-acid (p. 175). When ethyl iodide acts upon sodium arsenite, AsO_3Na_3, sodium monoethyl arsonate, $C_2H_5\,.\,AsO(ONa)_2$, is produced.

Dimethyl Arsine Derivatives.—Cacodylic oxide or *alkarsine*, $\begin{matrix}(CH_3)_2As \\ (CH_3)_2As\end{matrix}\!>\!O$, is the starting-out material for the preparation of the dimethyl compounds. Its formation from potassium acetate and arsenic trioxide has already been given on p. 176. The crude oxide ignites spontaneously in the air. This is due to the presence in it of a slight amount of free cacodyl. When prepared from *cacodyl chloride* by caustic potash it does not inflame spontaneously, and is a liquid with a stupefying odor. It solidifies at —25°. It boils at 120°, and at 15° has a specific gravity of 1.462. It is insoluble in water, but readily soluble in alcohol and in ether.

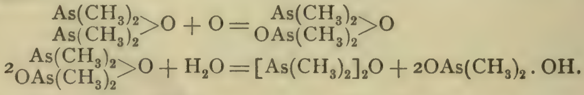
Dimethyl Arsine, *Cacodyl Hydride*, $(CH_3)_2AsH$, boils at 36°. It is produced when zinc and hydrochloric acid act upon cacodyl chloride in alcoholic solution. It is a colorless, mobile liquid, with the characteristic cacodyl odor. It inflames spontaneously in the air (B. **27**, 1378).

Cacodyl Chloride, $As(CH_3)_2Cl$, is formed by heating trimethyl arsen-dichloride, $As(CH_3)_3Cl_2$ (see above) and by acting upon cacodyl oxide with hydrochloric acid, as well as from Cl_2 and cacodyl. It is more readily obtained by heating the corrosive sublimate compound of the oxide with hydrochloric acid. It boils at 100°. It unites with chlorine to form the *trichloride*, $As(CH_3)_2Cl_3$, which renders possible the transition from the dimethyl compounds to the monomethyl derivatives.

Cacodyl Sulphide, $\begin{matrix}As(CH_3)_2\\As(CH_3)_2\end{matrix}\!>\!S$, from cacodyl chloride and barium sulphide, inflames in the air.

Cacodyl Cyanide, $As(CH_3)_2 . CN$, is formed by heating cacodyl chloride with mercuric cyanide. It fuses at 33° and boils at 140°.

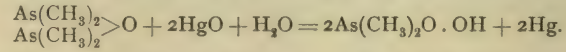
Cacodylic Acid, $(CH_3)_2AsO . OH$ (see p. 175), corresponds in its composition to dimethyl phosphinic acid. Cacodyl oxide, by slow oxidation, passes into cacodyl cacodylate, which breaks down, when distilled with water, into cacodylic oxide and cacodylic acid:



$$\begin{matrix}As(CH_3)_2\\As(CH_3)_2\end{matrix}\!>\!O + O = \begin{matrix}As(CH_3)_2\\OAs(CH_3)_2\end{matrix}\!>\!O$$

$$2\begin{matrix}As(CH_3)_2\\OAs(CH_3)_2\end{matrix}\!>\!O + H_2O = [As(CH_3)_2]_2O + 2OAs(CH_3)_2 . OH.$$

It is also obtained by the action of mercuric oxide upon cacodylic oxide:



$$\begin{matrix}As(CH_3)_2\\As(CH_3)_2\end{matrix}\!>\!O + 2HgO + H_2O = 2As(CH_3)_2O . OH + 2Hg.$$

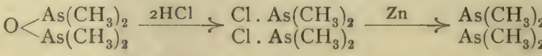
It is easily soluble in water, is odorless, and melts at 200°, with decomposition.

Hydriodic acid reduces it to cacodyl iodide, $As(CH_3)_2I$.

Hydrogen sulphide changes it to *cacodyl sulphide*.

PCl_5 converts it into *dimethyl arsentrichloride*, $(CH_3)_2AsCl_3$, which, like an acid chloride, regenerates cacodylic acid with water.

Cacodyl, $As_2(CH_3)_4 = \begin{matrix}As(CH_3)_2\\|\\As(CH_3)_2\end{matrix}$, diarsentetramethyl, is formed by heating the chloride with zinc filings in an atmosphere of carbon dioxide:



$$O\!<\!\begin{matrix}As(CH_3)_2\\As(CH_3)_2\end{matrix} \xrightarrow{2HCl} \begin{matrix}Cl . As(CH_3)_2\\Cl . As(CH_3)_2\end{matrix} \xrightarrow{Zn} \begin{matrix}As(CH_3)_2\\As(CH_3)_2\end{matrix}.$$

It is a colorless liquid, insoluble in water. It boils at 170°, and solidifies at —6°. Its odor is frightfully strong, and may induce vomiting. Cacodyl takes fire very readily in the air and burns to As_2O_3, carbon dioxide and water. It yields cacodyl chloride with chlorine and the sulphide with sulphur. Nitric acid converts it into a nitrate, $As(CH_3)_2 . O . NO_2$.

Ethyl Cacodyl, $\begin{matrix}As(C_2H_5)_2\\|\\As(C_2H_5)_2\end{matrix}$, diethylarsine, is formed together with triethylarsine on heating sodium arsenide with ethyl iodide. It boils at 185–190°, and takes fire in the air. It oxidizes to *diethyl arsinic acid*, $(C_2H_5)_2AsO . OH$.

TERTIARY ARSINES.

The tertiary arsines are formed by the action of the zinc alkyls upon arsenic trichloride and by heating the alkyl iodides with sodium arsenide.

Cacodyl, formed simultaneously, is separated by fractional distillation.

Trimethylarsine, $(CH_3)_3As$, and **Triethylarsine,** $(C_2H_5)_3As$, are liquids with very disagreeable odor. With oxygen they yield *Trimethyl arsenoxide*, $(CH_3)_3AsO$, and *Triethyl arsenoxide*, $(C_2H_5)_3AsO$. These bodies correspond to *triethylamine oxide* (p. 172) and *triethyl phosphine oxide* (p. 175); with sulphur they yield *trimethyl-* and *triethyl arsine sulphide*, $As(C_2H_5)_3S$; and with Br_2 and I_2 they form *trimethyl arsine bromide*, $As(CH_3)_3Br_2$, and *triethyl arsine iodide*, $As(C_2H_5)_3I_2$.

Quaternary Alkyl Arsonium Derivatives. — *Tetramethyl Arsonium Iodide*, $As(CH_3)_4I$, and *tetra-ethyl arsonium iodide*, $As(C_2H_5)_4I$, are obtained by the union of trimethyl arsine and triethyl arsine with methyl iodide and ethyl iodide. Both bodies crystallize, and correspond to the tetra-alkyl ammonium and phosphonium iodides (pp. 168, 174). Like the latter, they are changed by moist silver oxide to hydroxides:

Tetramethyl Arsonium Hydroxide, $As(CH_3)_4OH$, and *Tetra-ethyl Arsonium Hydroxide*, $As(C_2H_5)_4OH$.

These are crystalline, deliquescent bodies. They show a strong alkaline reaction.

8. ALKYL DERIVATIVES OF ANTIMONY.

The derivatives of antimony and the alkyls are perfectly analogous to those of arsenic; but those containing one and two alkyl groups do not exist. We are indebted to Löwig and to Landolt for our knowledge of them.

Tertiary Stibines are produced like the tertiary arsines:

(1) By the action of alkyl iodides upon potassium or sodium antimonides;

(2) By the interaction of zinc alkyls and antimony trichloride.

Trimethylstibine, $Sb(CH_3)_3$, antimony trimethyl, boils at 81°; its sp. gr. at 15° is 1.523, and **Triethylstibine or Stibethyl**, $Sb(C_2H_5)_3$, boiling at 159°, are liquids which take fire in the air, and are insoluble in water. In all their reactions they manifest the character of a bivalent metal, perhaps calcium or zinc. With oxygen, sulphur, and the halogens, they combine energetically and decompose the concentrated haloid acids, expelling their hydrogen:

$$Sb(C_2H_5)_3 + 2HCl = Sb(C_2H_5)_3Cl_2 + H_2.$$

Triethyl Stibine Oxide, $Sb(C_2H_5)_3O$, is soluble in water, which is also true of *Triethylstibine Sulphide*, $Sb(C_2H_5)_3S$, consisting of shining crystals. Its solution behaves somewhat like a calcium sulphide solution. It precipitates sulphides from solutions of the heavy metals with the formation of salts of triethylstibine.

Quaternary Stibonium Compounds, prepared from tertiary stibines by the addition of alkyl iodides, are changed by moist silver oxide into *tetra-alkyl stibonium hydroxides*. *Tetramethyl* and *Tetraethyl stibonium iodide*, $Sb(C_2H_5)_4I$, as well as *Tetramethyl* and *Tetraethyl stibonium hydroxide*, $(C_2H_5)_4SbOH$, resemble the corresponding arsenic derivatives very much in their properties.

9. ALKYL COMPOUNDS OF BISMUTH.

These arrange themselves with those derived from antimony and arsenic; but in accordance with the complete metallic nature of bismuth, we do not meet any compounds here analogous to stibonium or arsonium.

Further, in trialkyl derivatives the alkyl groups are less intimately united with the bismuth than they are with arsenic and antimony in their corresponding derivatives.

Tertiary bismuthides result from (1) the action of alkyl iodides upon potassium bismuthide; (2) the interaction of zinc alkyls and bismuth tri-bromide.

Bismuth-Trimethyl, $Bi(CH_3)_3$, and **Bismuth-Triethyl**, $Bi(C_2H_5)_3$, are liquids. They can be distilled without decomposition under diminished pressure. They explode when heated at the ordinary pressure (B. **20**, 1516; **21**, 2035). Bismuth trimethide is changed by hydrochloric acid to $BiCl_3$ and *methane*. The tri-ethide is spontaneously inflammable. It unites with iodine to *Bismuth Diethyl Iodide*, $Bi(C_2H_5)_2I$; and with mercuric chloride to **Bismuth-ethyl Chloride**, $Bi(C_2H_5)Cl_2$:

$$Bi(C_2H_5)_3 + 2HgCl_2 = Bi(C_2H_5)Cl_2 + 2Hg(C_2H_5)Cl.$$

From the alcoholic solution of the iodide the alkalies precipitate *Bismuth-ethyl oxide*, $Bi(C_2H_5)O$ an amorphous, yellow powder, which takes fire readily in the air. The *nitrate*, $Bi(C_2H_5){<}\begin{matrix}O.NO_2\\O.NO_2\end{matrix}$, is produced by adding silver nitrate to the iodide.

10. BORON ALKYL COMPOUNDS.

These are formed by the action of zinc alkyls upon (1) boron trichloride, (2) boric ethyl ester (p. 147) (Frankland, A. **124**, 129):

$$2B(O.C_2H_5)_3 + 3Zn(C_2H_5)_2 = 2B(C_2H_5)_3 + 3(C_2H_5 . O)_2Zn.$$

Trimethyl Borine is a gas.

Triethylborine, or Borethyl, $B(C_2H_5)_3$, boils at 95°. Both ignite in contact with the air and possess an extremely penetrating odor. When heated together with hydrochloric acid, ethyl borine decomposes into diethylborine chloride and ethane:

$$B(C_2H_5)_3 + HCl = B(C_2H_5)_2Cl + C_2H_6.$$

Slowly oxidized in the air, triethylborine passes into the diethyl ester of ethyl boric acid or **Boron Etho-diethoxide**, $B(C_2H_5)(O.C_2H_5)_2$, boiling at 125°; water decomposes it into ethyl boric acid, $C_2H_5.B(OH)_2$.

11. SILICON ALKYL COMPOUNDS.

Silicon is the nearest analogue of carbon. Its similarity to the latter shows itself very strongly in its derivatives with the alcohol radicals, which in many respects resemble the correspondingly constituted paraffins (Friedel; Crafts; Ladenburg, A. **203**, 241). As early as 1863 Wöhler directed attention to the analogy existing between the carbon and silicon compounds.

Silicon Tetramethide, $Si (CH_3)_4$, corresponds to *Tetramethyl Methane*, $C(CH_3)_4$.

Silicon Tetraethide, $Si(C_2H_5)_4$, corresponds to *Tetraethyl Methane*, $C(C_2H_5)_4$.

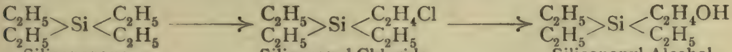
They are produced like the alkyl borines when zinc alkyls act upon

(1) Silicon halogen compounds;

(2) Upon esters of silicic acid.

Silicon-methyl, $Si(CH_3)_4$, from $SiCl_4$ and zinc methyl, boils at 30°.

Silicon-ethyl, Silicon-tetraethide, $Si(C_2H_5)_4$, *Silicononane*, from $SiCl_4$ and $Zn(C_2H_5)_2$, by the action of chlorine, forms a substitution product, $Si\left\{\begin{matrix}(C_2H_5)_3\\C_2H_4Cl\end{matrix}\right.$, silicononyl chloride. Potassium acetate changes this to the acetic ester of silicononyl alcohol, which alkalies decompose into acetic acid and **silicononyl alcohol**:



$$\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!>Si<\!\begin{matrix}C_2H_5\\C_2H_5\end{matrix} \longrightarrow \begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!>Si<\!\begin{matrix}C_2H_4Cl\\C_2H_5\end{matrix} \longrightarrow \begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!>Si<\!\begin{matrix}C_2H_4OH\\C_2H_5\end{matrix}$$

Silicononane, B. P. 153° — **Silicononyl Chloride,** B. P. 185° — **Silicononyl Alcohol.** B. P. 190°.

Silicon Hexethyl, or **Hexethyl-silicoethane,** $Si_2(C_2H_5)_6$, from zinc ethyl and Si_2I_6, boils from 250–253°.

Triethylsilicon Ethylate, $(C_2H_5)_3\overset{IV}{Si}.O.C_2H_5$, boils at 153°.

Diethylsilicon-diethylate, $(C_2H_5)_2Si.(O.C_2H_5)_2$, boils at 155.8°.

Ethylsilicon-triethylate, $(C_2H_5)Si(O.C_2H_5)_3$, is a liquid with a camphor-like odor, boiling at 159°. These three compounds are produced when zinc ethide acts upon silicic ethyl ester, $Si(OC_2H_5)_4$ (p. 147).

Acetic anhydride converts triethyl silicon ethyl ester into an acetic ester. When this is saponified by caustic potash, it yields *Triethylsilicon hydroxide* or *Triethyl silicol*, $(C_2H_5)_3Si.OH$, corresponding in constitution to *Triethyl carbinol.*

Acetyl chloride changes diethyl silicon diethyl ester into *Diethylsilicon chloride*, $(C_2H_5)_2SiCl_2$, boiling at 148°. Water transposes it into *diethylsilicon oxide*, $(C_2H_5)_2$-$Si.O$, corresponding to diethyl ketone in composition.

With acetyl chloride ethyl silicon triethyl ester *forms ethyl silicon trichloride*, $(C_2H_5)SiCl_3$. This liquid fumes strongly in the air, boils at about 100°, and when treated with water passes into ethyl silicic acid, $(C_2H_5)SiO.OH$ (Silico-propionic acid), which is analogous to propionic acid, $C_2H_5.CO.OH$, in constitution. It is a white, amorphous powder, which becomes incandescent when heated in the air. With the corresponding propionic acid it only shares the property of being an acid.

TABLE.

$(C_2H_5)_3SiOH$,	Triethyl Silicol	corresponds to	$(C_2H_5)_3C.OH$,	Triethyl Carbinol.
$(C_2H_5)_2SiO$,	Diethyl Silicon Oxide	corresponds to	$(C_2H_5)_2CO$,	Diethyl Ketone.
$C_2H_5.SiO.OH$,	Silico-propionic Acid	corresponds to	$C_2H_5.COOH$,	Propionic Acid.

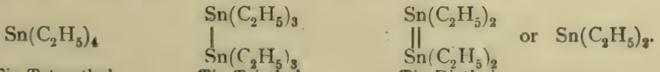
12. GERMANIUM ALKYL DERIVATIVES.

The compounds of germanium form the transition from those of silicon to those of tin.

Germanium-Ethide, $Ge(C_2H_5)_4$, is formed when zinc ethide acts upon germanium chloride. It is a liquid with a leek-like odor. It boils at 160° (Cl. Winkler, J. pr. Ch. [2] 36, 204).

13. TIN ALKYL COMPOUNDS.

In addition to the saturated derivatives with four alkyls, *tin* is also capable of uniting with three and two alkyls, forming:



$$Sn(C_2H_5)_4 \qquad \begin{matrix}Sn(C_2H_5)_3\\ |\\ Sn(C_2H_5)_3\end{matrix} \qquad \begin{matrix}Sn(C_2H_5)_2\\ \|\\ Sn(C_2H_5)_2\end{matrix} \text{ or } Sn(C_2H_5)_2.$$

Tin Tetraethyl — **Tin Triethyl** — **Tin Diethyl.**

The alkyl derivatives of tin were studied by Löwig, Cahours, Ladenburg, and others. The reactions resorted to in order to combine tin with alkyls are the same as were employed with arsenic, antimony, and other elements. (1) The action of zinc alkyls upon stannic chloride, when $Sn(CH_3)_4$ and $Sn(C_2H_5)_4$ are produced. (2) The action of alkyl iodides upon tin-sodium (tin alone or tin-zinc). When the alloy contains a great deal of sodium, $Sn(C_2H_5)_3$ is produced, but when comparatively little sodium is present the chief product is $Sn(C_2H_5)_2I_2$. Sodium abstracts iodine from both of the primarily formed iodides with the formation of $Sn_2(C_2H_5)_4$ and $Sn_2(C_2H_5)_6$. These can be separated by means of alcohol, in which the latter is insoluble.

Tin Tetramethyl, $Sn(CH_3)_4$, boils at 78°. **Tin Tetraethyl, Stannic Ethide**, $Sn(C_2H_5)_4$, boils at 181° and possesses a specific gravity of 1.187 at 23°. Both are colorless, ethereal smelling liquids, insoluble in water. By the action of the halogens the alkyls are successively eliminated. Hydrochloric acid acts similarly:

$$\begin{aligned} Sn(C_2H_5)_4 + I_2 &= Sn(C_2H_5)_3I + C_2H_5I, \text{ etc.} \\ Sn(C_2H_5)_4 + HCl &= Sn(C_2H_5)_3Cl + 2C_2H_6, \text{ etc.} \end{aligned}$$

The alkyl groups are not so firmly united in the zinc alkyls as they are in the alkyls of silicon.

Tin Triethyl Iodide, $Sn(C_2H_5)_3I$, boils at 231°, and has a specific gravity of 1.833 at 22°. *Tin triethyl chloride*, $Sn(C_2H_5)_3Cl$, boils at from 208–210°, and has a specific gravity of 1.428. Alcohol is a solvent for both. When either one is acted upon by silver oxide or caustic potash, there is produced:

Tin Triethyl Hydroxide, $Sn(C_2H_5)_3.OH$, melting at 66° and boiling at 272°. It volatilizes along with the steam. It is sparingly soluble in water, but dissolves readily in alcohol and ether. It reacts strongly alkaline, and yields crystalline salts with the acids, *e. g.*, $Sn(C_2H_5)_3.O.NO_2$. When the hydroxide is heated for some time to almost the boiling temperature, it breaks down into water and *tin triethyl oxide*, $\begin{matrix}Sn(C_2H_5)_3\\Sn(C_2H_5)_3\end{matrix}>O$, an oily liquid, which in the presence of water at once regenerates the hydrate.

Tin Triethyl, $Sn_2(C_2H_5)_6$ (see above), is a liquid, of mustard-like odor, insoluble in alcohol, but readily soluble in ether. It distils with slight decomposition at 265–270°. It combines with oxygen, forming tin-triethyl oxide, $\begin{matrix}Sn(C_2H_5)_3\\Sn(C_2H_5)_3\end{matrix}>O$, and with iodine yields tin-triethyl iodide, $2Sn(C_2H_5)_3I$.

Tin Diethyl, $Sn_2(C_2H_5)_4$, or $Sn(C_2H_5)_2$, is a thick oil, decomposing when heated into $Sn(C_2H_5)_4$ and tin. It combines with oxygen and the halogens.

Tin Diethyl Chloride, $Sn(C_2H_5)_2Cl_2$, melts at 85° and boils at 220°. The *iodide*, $Sn(C_2H_5)_2I_2$, fuses at 44.5°, and boils at 245°.

Ammonium hydroxide and the alkalies precipitate from aqueous solutions of both the halogen compounds:

Tin Diethyl Oxide, $Sn(C_2H_5)_2O$, a white, insoluble powder. It is soluble in excess of alkali, and forms crystalline salts with the acids, *e. g.*, $Sn(C_2H_5)_2<\begin{matrix}O.NO_2\\O.NO_2\end{matrix}$.

14. METALLO-ORGANIC COMPOUNDS.

The metallo-organic compounds are those resulting from the union of metals with univalent alkyls; those with the bivalent alkylens, C_nH_{2n}, have not yet been prepared. Inasmuch as we have no marked line of difference between metals and non metals, the metallo-organic derivatives attach themselves, on the one side, by the derivatives of antimony and arsenic, to the phosphorus and nitrogen bases; and on the other, through the selenium compounds, to the sulphur alkyls and ethers; whereas the lead derivatives approach those of tin, and the latter approach the silicon alkyls and the hydrocarbons.

Upon examining the metals as they arrange themselves in the periodic system it is rather remarkable to find that it is only those which attach themselves to the electro-negative non-metals which are capable of yielding alkyl derivatives. In the three large periods this power manifests and extends itself only as far as the group of zinc (Zn, Cd, Hg). (Compare *Inorganic Chemistry.*)

Those compounds in which the metals present their maximum valence, *e. g.*,

$$\overset{II}{Hg}(CH_3)_2 \qquad \overset{III}{Al}(CH_3)_3 \qquad \overset{IV}{Sn}(CH_3)_4 \qquad \overset{IV}{Pb}(CH_3)_4 \qquad \overset{V}{Sb}(CH_3)_5,$$

are volatile liquids, usually distilling undecomposed in vapor form; therefore, the determination of their vapor density is an accurate means of establishing their molecular weight, and the valence of the metals.

The behavior of the metallo-organic radicals, derived from the molecules by the separation of single alkyls, is especially noteworthy. The univalent radicals, *e. g.*,

$$\overset{II}{Hg}(CH_3)— \quad \overset{III}{Tl}(CH_3)_2— \quad \overset{IV}{Sn}(CH_3)_3— \quad \overset{IV}{Pb}(CH_3)_3— \quad \overset{V}{Sb}(CH_3)_4—,$$

show great resemblance to the alkali metals in all their derivatives. Like other univalent radicals, they cannot be isolated. They yield hydroxides, *e. g.*,

$$Hg(C_2H_5).OH \qquad Tl(CH_3)_2.OH \qquad Sn(CH_3)_3.OH,$$

perfectly similar to KOH and NaOH. Some of the univalent radicals, when separated from their compounds, double themselves:

$$\begin{array}{c}As(CH_3)_2\\ |\\ As(CH_3)_2\end{array} \qquad \begin{array}{c}Si(CH_3)_3\\ |\\ Si(CH_3)_3\end{array} \qquad \begin{array}{c}Sn(CH_3)_3\\ |\\ Sn(CH_3)_3\end{array} \qquad \begin{array}{c}Pb(CH_3)_3\\ |\\ Pb(CH_3)_3.\end{array}$$

By the exit of two alkyls from the saturated compounds, the bivalent radicals result:

$$=\overset{III}{Bi}(CH_3) \qquad =\overset{IV}{Te}(CH_3)_2 \qquad =\overset{IV}{Sn}(C_2H_5)_2 \qquad =\overset{V}{Sb}(CH_3)_3.$$

In their compounds (oxides and salts) these resemble the bivalent alkaline earth metals, or the metals of the zinc group. A few of them occur in free condition. As unsaturated molecules, however, they are highly inclined to saturate two affinities directly. Antimony triethyl, $Sb(C_2H_5)_3$ (see p. 177), and apparently, too, tellurium diethyl, $Te(C_2H_5)_2$, have the power of uniting with acids to form salts; hydrogen is liberated at the same time. This would indicate a distinct metallic character.

Finally, the trivalent radicals, like $\overset{V}{As}(CH_3)_2$, can also figure as univalent. This is the case, too, with vinyl, C_2H_3. These may be compared to aluminium, and the so-called cacodylic acid, $As(CH_3)_2O.OH$ (p. 178), to aluminium metahydrate, AlO.OH.

We conclude, therefore, that the electro-negative metals, by the successive union of alcohol radicals, always acquire a more strongly impressed basic, alkaline character. This also finds expression with the non-metals (sulphur, phosphorus, arsenic, etc.). (Compare pp. 148, 173, 175.)

The first metallo-organic derivatives were prepared by Frankland. *Zinc alkyls* are particularly important as carriers of alcohol radicals.

Methods of Formation:

(1) Action of metals (Mg, Zn, Hg) upon alkyl iodides.

(2) Action of alloys (Pb, Na) upon alkyl iodides (see Bi-, Sb-, Sn-compounds).

(3) Action of metals (K, Na, Be, Al) upon metallo organic bodies (zinc alkyls, mercury alkyls).

(4) Action of metallic chlorides ($PbCl_2$) on metallo organic derivatives (zinc alkyls; compare BCl_3, $SiCl_4$, $SnCl_4$, $GeCl_4$ upon zinc alkyls).

A. COMPOUNDS OF THE ALKALI METALS.

When sodium or potassium is added to zinc methide or ethide, zinc separates at the ordinary temperature, and from the solution which is thus produced, crystalline compounds deposit on cooling. The liquid retains a great deal of unaltered zinc alkyl, but it also appears to contain the sodium and potassium compounds—at least it sometimes reacts quite differently from the zinc alkyls. Thus, it absorbs carbon dioxide, forming salts of the fatty acids (Wanklyn, A. 111, 234):

$$C_2H_5Na + CO_2 = \underset{\text{Sodium Propionate.}}{C_2H_5 . CO_2Na.}$$

These decomposable bodies cannot be separated in a pure condition.

B. COMPOUNDS OF THE METALS OF THE MAGNESIUM GROUP.

1. **Beryllium Ethide**, $Be(C_2H_5)_2$, formed by the 3d method, boils at from 185°–188° and ignites spontaneously. **Beryllium Propyl**, $Be(C_3H_7)_2$, boils at 245°.

2. **Magnesium Ethide**, $Mg(C_2H_5)_2$. On warming magnesium filings with ethyl iodide away from contact with the air, magnesium ethyl iodide, $Mg{<}^{C_2H_5}_{I}$, first results. On applying heat to this it decomposes into $Mg(C_2H_5)_2$ and MgI_2 (B. 25, R. 745; 26, R. 718). $Be(C_2H_5)_2$ and $Mg(C_2H_5)_2$, like $Zn(C_2H_5)_2$ (see this), are decomposed by water.

C. ZINC ALKYL COMPOUNDS.

Zinc methide and zinc ethide were discovered in 1849 by Frankland (A. 71, 213; 85, 329; 99, 342). The zinc alkyls are exceedingly reactive, and are, on this account, the most important class of the metallic alkyls.

Methods of Formation.—(1) When zinc filings act upon iodides of the alcohol radicals in sunlight, iodides are formed, which are decomposed by heat into zinc alkyls and zinc iodide:

$$C_2H_5I + Zn = I{-}Zn{-}C_2H_5$$

$$2Zn{<}^{C_2H_5}_{I} = Zn(C_2H_5)_2 + ZnI_2.$$

The action may be accelerated if the zinc turnings have been previously corroded, or by the application of zinc-sodium or zinc-copper. In preparing zinc ethide, ethyl iodide is poured over zinc clippings and a little pure zinc ethide is then added. The formation of I—Zn . C_2H_5 is then completed at the ordinary temperature, and this body separates in large, transparent crystals. When it is heated in a current of CO_2, it yields zinc ethide (A. **152**, 220; B. **26**, R. 88).

(2) The mercury alkyls are transposed by zinc into zinc alkyls, with the separation of mercury:

$$Hg(C_2H_5)_2 + Zn = Zn(C_2H_5)_2 + Hg.$$

Properties.—The zinc alkyls are colorless, disagreeable-smelling liquids, fuming strongly in the air and igniting readily; therefore, they can only be handled in an atmosphere of carbon dioxide. They inflict painful wounds when brought in contact with the skin.

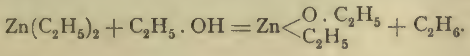
Zinc Methide, $Zn(CH_3)_2$, boils at 46°. Its sp. gr. at 10° is 1.386.
Zinc Ethide, $Zn(C_2H_5)_2$. boils at 118°, and has the sp. gr. 1.182 at 18°.
Zinc Propyl, $Zn(CH_2 . CH_2 . CH_3)_2$, boils at 146°.
Zinc Isopropyl, $Zn(C_3H_7)_2$, boils at 136–137° (B. **26**, R. 380).
Zinc Isobutyl, $Zn(C_4H_9)_2$, boils at 165–167° (A. **223**, 168).
Zinc Isoamyl, $Zn(C_5H_{11})_2$, boils at 210° (A. **130**, 122).

Transpositions.—The zinc alkyls are exceedingly reactive.

(1) Water decomposes them very energetically, forming hydrocarbons and zinc hydroxide (see Methane, Ethane, pp. 81, 82).

(2) Oxygen is added by slow oxidation in the air, and compounds, *e. g.*, $(CH_3)_2$-ZnO_2, analogous to peroxides, are produced. These explode readily and liberate iodine from potassium iodide (B. **23**, 394).

(3) The alcohols convert the zinc alkyls into zinc alcoholates and hydrocarbons:



$$Zn(C_2H_5)_2 + C_2H_5 . OH = Zn\begin{matrix}\diagup O . C_2H_5 \\ \diagdown C_2H_5\end{matrix} + C_2H_6.$$

(4) The free halogens decompose both the zinc alkyls and those of other metals very energetically:

$$Zn(C_2H_5)_2 + 2Br_2 = 2C_2H_5Br + ZnBr_2.$$

(5) They react with chlorides of the heavy metals and the non-metals, whereby alkyl derivatives of the latter are produced (p. 184).

(6) The zinc alkyls absorb sulphur dioxide and become zinc salts of the sulphinic acids (p. 153).

(7) Nitric oxide dissolves in zinc diethyl and forms a crystalline compound, from which the zinc salt of the so-called *dinitroethylic acid*, $C_2H_5 . N_2O_2H$, is obtained by the action of water and CO_2.

The application of the zinc alkyls—zinc methide and zinc ethide—is particularly important in nucleus-synthetic reactions:

(1) Hydrocarbons are formed when the alkyl iodides are exposed to high temperatures (p. 84).

(2) When zinc alkyls (zinc and alkyl iodides) act upon aldehydes, acid chlorides, ketones, formic esters, acetic esters, and chlorinated ethers, derivatives of *secondary*, *tertiary*, and *primary* alcohols, as well as of *ketones*, are produced. The alcohols (pp. 113, 114) and ketones (p. 209) can easily be obtained from them.

The alkyl oxides and the alkylen oxides are, however, not affected by the zinc alkyls (B. **17**, 1968).

D. MERCURY ALKYL DERIVATIVES.

The *dialkyl compounds* are formed—

(1) By the interaction of sodium amalgam and alkyl iodides, with the addition of acetic ester (Frankland, A. 130, 105, 109). The rôle of the acetic ester in this reaction has not yet been explained:

$$2C_2H_5I + Hg . Na_2 = (C_2H_5)_2Hg + 2NaI.$$

(2) By the action of potassium cyanide upon mercury alkyl iodides.

(3) By the action of zinc alkyls upon mercury alkyl iodides:

$$2C_2H_5HgI + Zn(C_2H_5)_2 = 2(C_2H_5)_2Hg + ZnI_2.$$

(4) By the action of zinc alkyls upon mercuric chloride:

$$HgCl_2 + Zn(C_2H_5)_2 = (C_2H_5)_2Hg + ZnCl_2.$$

Properties.—These compounds are colorless, heavy liquids, possessing a faint, peculiar odor. Their vapors are extremely poisonous. Water and air occasion no change in them, but when heated they ignite easily.

Mercury Methide, $Hg(CH_3)_2$, sp. gr. 3.069, boils at 95°. *Mercury Ethide*, $Hg(C_2H_5)_2$, sp. gr. 2.44, boils at 159° and at 200° breaks down into Hg and butane, $C_2H_5 . C_2H_5$. It yields ethane (p. 82) when treated with concentrated sulphuric acid.

The *mono-alkyl derivatives* arise (1) by the action of mercury upon alkyl iodides in sunlight: $C_2H_5I + Hg = C_2H_5 . Hg . I$; (2) from the dialkyl mercury derivatives—(*a*) by the action of halogens; (*b*) by the action of the haloid acids; (*c*) by the action of mercuric chloride.

Mercury Methyl Iodide, CH_3HgI, forms shining needles, insoluble in water, melting at 143°. Silver nitrate changes it to *methyl mercury nitrate*, $CH_3Hg . O . NO_2$. *Mercury Ethyl Iodide*, C_2H_5HgI, is decomposed, by sunlight, into mercuric iodide and C_4H_{10}. *Mercury Allyl Iodide*, C_3H_5HgI, melts at 135° and is converted by HI into propylene and mercuric iodide, HgI_2. Moist silver oxide changes the haloid derivatives to *hydroxyl compounds:*

$$C_2H_5HgCl + (AgOH) = C_2H_5 . Hg . OH + AgCl.$$

Ethyl Mercuric Hydroxide, C_2H_5HgOH, is a thick liquid, soluble in water and in alcohol. It reacts strongly alkaline, and forms salts with acids.

E. ALKYL COMPOUNDS OF THE METALS OF THE ALUMINIUM GROUP.

The aluminium alkyl derivatives attach themselves to those springing from boron (p. 180). They are produced by the action of the mercury alkyls upon aluminium filings.

Aluminium-Trimethyl, $Al(CH_3)_3$, boils at 130°. **Aluminium Triethyl**, $Al(C_2H_5)_3$, boils at 194°. Both are colorless liquids and are spontaneously inflammable. Water decomposes them with great violence, forming methane (ethane) and aluminium hydroxide. Their vapor densities answer better for the molecular formula $Al(C_2H_5)_3$ than for $Al_2(CH_3)_6$ (see B. 22, 551; Z. phys. Ch. 3, 164).

The derivatives of trivalent gallium and indium have not been prepared.

The thallium-diethyl compounds are known.

Thallium-Diethyl Chloride, $Tl(C_2H_5)_2Cl$, is formed when zinc ethide is allowed to act upon thallium chloride.

Thallium-diethyl salts, *e. g.*, $Tl(C_2H_5)_2O . NO_2$, are obtained from this by double decomposition with silver salts. If the sulphate be decomposed with barium hydrate, *thallium-diethyl hydroxide*, $Tl(C_2H_5)_2 . OH$, is obtained. This is readily soluble in water, crystallizes therefrom in glistening needles, and has a strong alkaline reaction.

F. ALKYL COMPOUNDS OF LEAD.

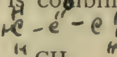
These are very similar to the derivatives of tin (p. 181). Derivatives containing two alkyl groups combined with one atom of lead do not exist. In these the lead, as in most of its inorganic derivatives, would be bivalent. Lead alkyls are produced (1) by acting upon lead chloride with zinc ethide: $Pb(C_2H_5)_4$; (2) by the interaction of alkyl iodides and lead-sodium: $Pb_2(C_2H_5)_6$.

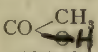
Lead Tetramethide, $Pb(CH_3)_4$, boils at 110°. *Lead Tetraethide*, $Pb(C_2H_5)_4$, and *Lead Triethide*, $Pb_2(C_2H_5)_6$, are oily liquids which cannot be distilled without decomposition. The *iodide*, $Pb(C_2H_5)_3I$, is produced when iodine acts upon lead tetraethide. On heating with moist silver oxide, *lead triethyl hydroxide*, $Pb(C_2H_5)_3 . OH$, distils over. This reacts very alkaline, and forms crystalline salts with the acids. The *sulphate*, $[Pb(C_2H_5)_3]_2SO_4$, dissolves in water with difficulty.

2. ALDEHYDES AND 3. KETONES.

When the derivatives of the methane hydrocarbons containing oxygen were discussed, attention was directed to the intimate genetic relations existing on the one hand between the primary alcohols, the aldehydes and mono carboxylic acids, and on the other between the secondary alcohols and the ketones (p. 108).

Aldehydes and ketones contain the carbonyl group CO, which in the latter unites two alkyls, but in the former is combined with only one alkyl and one hydrogen atom:

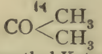




$$CO\!<\!\begin{smallmatrix}CH_3\\ H\end{smallmatrix}$$

Aldehyde

$CH_3C\begin{smallmatrix}=O\\ H\end{smallmatrix}$



$$CO\!<\!\begin{smallmatrix}CH_3\\ CH_3\end{smallmatrix}$$

Dimethyl Ketone.

This expresses the similarity and the difference in character of aldehydes and ketones.

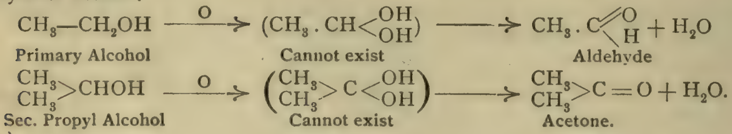
Aldehydes and ketones may be considered as the oxides of bivalent radicals, or as the anhydrides of *diacid alcohols*, or *glycols*, in which both hydroxyl groups are attached to the same terminal or intermediate carbon atom. Whenever the formation of dihydroxyl derivatives of the type $>C<\begin{smallmatrix}O-H\\ O-H\end{smallmatrix}$ might be expected, then, except in very rare instances, water separates, an *anhydride* is produced, and double union between carbon and oxygen follows, with the production of the carbonyl group $>C=O$. Ethers, however, of diacid alcohols, of the *ortho-aldehydes* and *ortho-ketones*, can exist, *e. g.*:

$$CH_3 . CH(O . C_2H_5)_2 \text{ and } CH_3 . C(O . C_2H_5)_2 . CH_3.$$

The following principal methods of formation are common to aldehydes and ketones:

(1) Oxidation of the alcohols, whereby the primary alcohols change to aldehydes and the secondary to ketones (p. 111).

In this oxidation an oxygen atom pushes itself between a hydrogen atom and the carbon atom to which the hydroxyl group is joined. In the moment of formation the expected diacid alcohol splits off water, and its anhydride results,—an aldehyde or ketone:

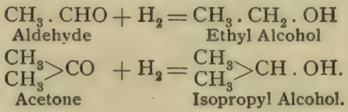


$$\underset{\text{Primary Alcohol}}{CH_3{-}CH_2OH} \xrightarrow{O} \underset{\text{Cannot exist}}{\left(CH_3\,.\,CH<{OH \atop OH}\right)} \longrightarrow \underset{\text{Aldehyde}}{CH_3\,.\,C{\nearrow O \atop \searrow H}} + H_2O$$

$$\underset{\text{Sec. Propyl Alcohol}}{{CH_3 \atop CH_3}\!>\!CHOH} \xrightarrow{O} \underset{\text{Cannot exist}}{\left({CH_3 \atop CH_3}\!>\!C<{OH \atop OH}\right)} \longrightarrow \underset{\text{Acetone.}}{{CH_3 \atop CH_3}\!>\!C=O} + H_2O.$$

By further oxidation the aldehydes become acids—*the hydrides of the acid radicals*,—while the ketones are decomposed.

Conversely, aldehydes and ketones again become primary and secondary alcohols by an addition of hydrogen:

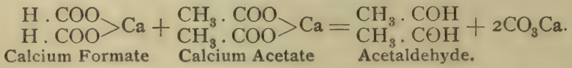


$$\underset{\text{Aldehyde}}{CH_3\,.\,CHO} + H_2 = \underset{\text{Ethyl Alcohol}}{CH_3\,.\,CH_2\,.\,OH}$$

$$\underset{\text{Acetone}}{{CH_3 \atop CH_3}\!>\!CO} + H_2 = \underset{\text{Isopropyl Alcohol.}}{{CH_3 \atop CH_3}\!>\!CH\,.\,OH.}$$

Because the aldehydes and ketones manifest an additive power with reference to hydrogen, they may be compared with compounds containing doubly linked carbon atoms, which also, by a dissolution of their double union, can add hydrogen. Compounds of this class having in their molecules carbon atoms which are doubly (or trebly) united, are in the more restricted sense called "*unsaturated carbon derivatives*" (p. 79). This idea may be extended, and all carbon derivatives having atoms of other elements in double or treble union with carbon, may be considered as "*unsaturated*." From this standpoint the aldehydes and ketones are unsaturated bodies (p. 38), and in fact most of the reactions of these two classes are due to the additive power of the unsaturated carbonyl group.

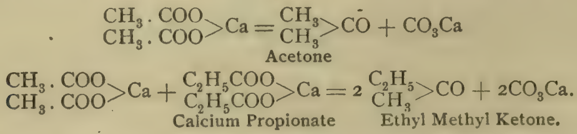
(2) The dry distillation of a mixture of the calcium, or better, barium salts of two monobasic fatty acids. Should in this case one of the acids be formic acid, aldehydes are produced:



$$\underset{\text{Calcium Formate}}{{H\,.\,COO \atop H\,.\,COO}\!>\!Ca} + \underset{\text{Calcium Acetate}}{{CH_3\,.\,COO \atop CH_3\,.\,COO}\!>\!Ca} = \underset{\text{Acetaldehyde.}}{{CH_3\,.\,COH \atop CH_3\,.\,COH}} + 2CO_3Ca.$$

It is the hydrogen of the formate which reduces the acid.

In all other instances ketones result, and they are either *simple*, with two similar alkyls, or *mixed*, with two dissimilar alkyls:



$${CH_3\,.\,COO \atop CH_3\,.\,COO}\!>\!Ca = \underset{\text{Acetone}}{{CH_3 \atop CH_3}\!>\!CO} + CO_3Ca$$

$${CH_3\,.\,COO \atop CH_3\,.\,COO}\!>\!Ca + \underset{\text{Calcium Propionate}}{{C_2H_5COO \atop C_2H_5COO}\!>\!Ca} = 2\underset{\text{Ethyl Methyl Ketone.}}{{C_2H_5 \atop CH_3}\!>\!CO} + 2CO_3Ca.$$

On extending this reaction to the calcium salts of adipic, pimelic and suberic acids, cyclo-paraffin ketones are produced.

2A. ALDEHYDES OF THE LIMIT SERIES, PARAFFIN ALDEHYDES, $C_nH_{2n+1}.CHO$.

The aldehydes exhibit in their properties a gradation similar to that of the alcohols. The lower members are volatile liquids, soluble in water, and have a peculiar odor, but the higher are solids, insoluble in water, and cannot be distilled without decomposition. In general they are more volatile and dissolve with more difficulty in water than the alcohols. In chemical respects the aldehydes are neutral substances.

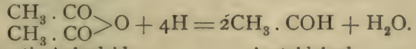
Formation.—(1) By the oxidation of primary alcohols, when the —$CH_2.OH$ group becomes —CHO (p. 188).

The above oxidation may be effected by oxygen; or air in presence of platinum sponge. It takes place more readily on warming the alcohols with potassium dichromate (or MnO_2) and dilute sulphuric acid (B. **5**, 699). Chlorine acts similarly in that it first oxidizes the primary alcohols, but then substitutes the alkyl groups of the aldehydes which have been formed (p. 197).

(2) By heating the calcium salts of fatty acids with calcium formate. This operation, when working with aldehydes which volatilize with difficulty, should be carried out under diminished pressure (p. 63) (B. **13**, 1413).

(3) By the action of nascent hydrogen (sodium amalgam, or, better, sodium upon the moist ethereal solution, B. **29**, R. 662) upon the chlorides of the acid radicals or their oxides, the acid anhydrides:

$$\underset{\text{Acetyl Chloride}}{CH_3.COCl} + 2H = \underset{\text{Acetaldehyde}}{CH_3.COH} + HCl$$

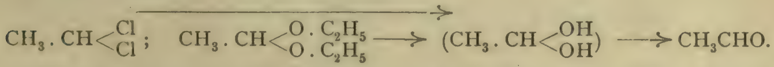


$$\underset{\text{Acetic Anhydride}}{\begin{matrix}CH_3.CO\\CH_3.CO\end{matrix}}\!\!>O + 4H = \underset{\text{Acetaldehyde.}}{2CH_3.COH} + H_2O.$$

In accordance with methods 2 and 3 the aldehydes may be viewed as ***hydrides of the acid radicals***.

(4) By heating the aldehyde chlorides with water alone, or with water and lead oxide.

(5) By the saponification of the ethereal and ester-derivatives, *e. g.*, *acetal*, $CH_3.CH<\begin{smallmatrix}OC_2H_5\\OC_2H_5\end{smallmatrix}$, and *ethidene diacetate*, $CH_3.CH<\begin{smallmatrix}O.CO.CH_3\\O.CO.CH_3\end{smallmatrix}$, with sulphuric acid or alkalies. From methods 4 and 5 dihydroxyl derivatives should be at first produced. These are the *glycols*, which, however, immediately pass into aldehydes with the simultaneous exit of water (p. 188):



$$CH_3.CH<\begin{smallmatrix}Cl\\Cl\end{smallmatrix};\quad CH_3.CH<\begin{smallmatrix}O.C_2H_5\\O.C_2H_5\end{smallmatrix} \longrightarrow (CH_3.CH<\begin{smallmatrix}OH\\OH\end{smallmatrix}) \longrightarrow CH_3CHO.$$

(6) When the sodium salts of mononitro-paraffins, having the nitro-group attached to a terminal carbon atom, are treated with acids, paraffin aldehydes are produced (B. **29**, 1223) (p. 156).

(7) Aldehydes can also be obtained from many addition products (p. 191), particularly the aldehyde ammonias and the alkali sulphite derivatives.

(8) When the *a*-mono-carboxylic acids are treated with sulphuric acid aldehydes are formed, with a simultaneous splitting-off of formic acid or its decomposition products—water and carbon monoxide:

$$\underset{\text{Lactic Acid}}{CH_3.CH(OH)CO_2H} = \underset{\text{Acetaldehyde}}{CH_3.CHO} + \underset{\text{Formic Acid.}}{H.COOH.}$$

Note.—Quite frequently aldehydes occur among the decomposition products of complex carbon compounds, as the result of their oxidation with MnO_2 and dilute sulphuric acid, or by means of a chromic acid solution.

Nomenclature and Isomerism.—Empirically, the aldehydes are distinguished from the alcohols by possessing two atoms less of hydrogen—hence their name, suggested by Liebig (from *Alkohol dehydrogenatus*), *e. g.*, ethyl aldehyde, propyl aldehyde, etc., etc. On account of their intimate relationship to the acids, their names are also derived from the latter, like acetaldehyde, propionic aldehyde, etc.

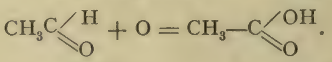
In the "Geneva nomenclature" the names of the aldehydes are formed from the corresponding saturated hydrocarbons by the addition of the suffix *al;* thus ethyl- or acetaldehyde would be termed [ethanal] (p. 57).

As there is an aldehyde corresponding to every primary alcohol, the number of isomeric aldehydes of definite carbon content equals the number of possible primary alcohols having the same carbon content (p. 109). The aldehydes are isomeric with the ketones, the unsaturated allyl alcohols, and the anhydrides of the ethylene-glycol series, containing an equal number of carbon atoms, *e. g.*:

$CH_3.CH_2.CHO$ isomeric with	$CH_3.CO.CH_3$	$CH_2=CHCH_2OH$	 $CH_2<{CH_2 \atop CH_2}>O.$
Propionic Aldehyde	Acetone	Allyl Alcohol	Trimethylene Oxide.

Transformations of the Aldehydes: A. *Reactions in which the carbon nucleus of the aldehydes remains the same.*

(1) Aldehydes, by oxidation, yield monocarboxylic acids with a like carbon content. *They are powerful reducing agents:*



$$CH_3C{\diagup H \atop \diagdown O} + O = CH_3—C{\diagup OH \atop \diagdown O}.$$

Their ready oxidation gives rise to important reactions serving for the detection and recognition of aldehydes. On adding an aqueous aldehyde solution to a weak ammoniacal silver nitrate solution, silver separates on the sides of the vessel as a brilliant mirror. Alkaline copper solutions are also reduced. A very delicate reaction of the aldehydes is their power of imparting an intense violet color to a fuchsine solution previously decolorized by sulphurous acid. The following is more sensitive: Add an aldehyde and a little sodium amalgam to the sodium hydroxide solution of diazobenzene sulphonic acid and a violet-red coloration is produced. (Compare further B. **14**, 675, 791, 1848; **15**, 1635, 1828; **16**, 657; **17**, R. 385.)

When oxygen or air is conducted through the hot solution of an aldehyde (like paraldehyde) in alcoholic potash, an intense light-display is observed in the dark; many aldehyde derivatives, and even grape sugar, deport themselves similarly (B. **10**, 321). Aldehydes absorb oxygen from the air. The oxygen in this solution, like ozone, can liberate iodine from a potassium iodide solution (B. **29**, 1454).

(2) Nearly all the aldehydes are converted into resin by the alkalies; some are transformed into acids and alcohols (this is especially true of the aromatic aldehydes), and others into acids and glycols (see these) by alcoholic alkali solutions:

$$2C_4H_9 . COH + KOH = C_4H_9 . CO . OK + C_4H_9 . CH_2 . OH.$$

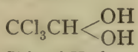
Amyl Aldehyde — Pot. Valerate — Amyl Alcohol.

The ease with which the double union of the carbon-oxygen atoms is broken is the cause of a large number of addition reactions, which are in part followed by an exit of water.

(3) Aldehydes, by the addition of nascent hydrogen, become *primary alcohols*, from which they are obtained by oxidation:

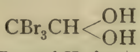
$$CH_3 . CHO + 2H = CH_3 . CH_2OH.$$

(4) *Deportment of the aldehydes toward water and alcohols.* (*a*) Ordinarily, aldehydes do not combine (compare p. 195; $CH_2(OH)_2$) with water. The polyhalide aldehydes, *e. g.*, *chloral*, *bromal*, *butyl chloral* (pp. 197, 198) do, however, have this power, and yield feeble and readily decomposable *hydrates*, representatives of diacid alcohols or glycols, *both* hydroxyl groups of which are attached to the *same* carbon atom:



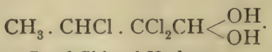
$$CCl_3CH\!<\!\begin{smallmatrix}OH\\OH\end{smallmatrix}$$

Chloral Hydrate
Trichlor-ethidene Glycol



$$CBr_3CH\!<\!\begin{smallmatrix}OH\\OH\end{smallmatrix}$$

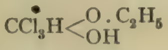
Bromal Hydrate



$$CH_3 . CHCl . CCl_2CH\!<\!\begin{smallmatrix}OH\\OH\end{smallmatrix}.$$

Butyl Chloral Hydrate.

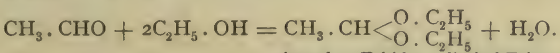
(*b*) It is also only the polyhalide aldehydes, *e.g.*, *chloral*, which unite with alcohols, forming *aldehyde-alcoholates*:



$$CCl_3H\!<\!\begin{smallmatrix}O . C_2H_5\\OH\end{smallmatrix}$$

Chloral Alcoholate.

(*c*) The ordinary aldehydes yield *acetals* with the alcohols at 100° (p. 200):

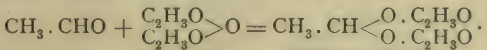


$$CH_3 . CHO + 2C_2H_5 . OH = CH_3 . CH\!<\!\begin{smallmatrix}O . C_2H_5\\O . C_2H_5\end{smallmatrix} + H_2O.$$

Acetal or Ethidene-diethyl Ether.

(5) *Behavior of the aldehydes with hydrogen sulphide and mercaptans*: (*a*) *hydrogen sulphide* and hydrochloric acid convert the aldehydes into *trithioaldehydes*: (*b*) with the *mercaptans* the aldehydes enter into an acetal synthesis after the addition of hydrochloric acid (p. 204).

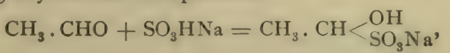
(6) Aldehydes and acid anhydrides unite to esters of the diacid alcohols or glycols, which are not stable in an isolated condition. Indeed, the aldehydes may be regarded as their anhydrides (pp. 188, 189):



$$CH_3 . CHO + \begin{smallmatrix}C_2H_3O\\C_2H_3O\end{smallmatrix}\!>\!O = CH_3 . CH\!<\!\begin{smallmatrix}O . C_2H_3O\\O . C_2H_3O\end{smallmatrix}.$$

Ethidene Diacetate.

(7) Aldehydes unite in a similar manner with acid alkaline sulphites, forming crystalline compounds:



$$CH_3 . CHO + SO_3HNa = CH_3 . CH\!<\!\begin{smallmatrix}OH\\SO_3Na\end{smallmatrix},$$

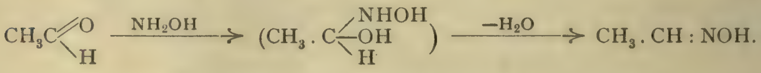
which may be regarded as salts of *oxysulphonic acids*. The aldehydes may be released from these salts by distillation with dilute sulphuric acid or soda. This procedure permits of the separation and purification of aldehydes from other substances.

(8) Behavior of aldehydes with ammonia, primary alkylamines, hydroxylamine, and phenylhydrazine ($C_6H_5 . NH . NH_2$). (*a*) They unite directly with ammonia to form crystalline compounds, called *aldehyde-ammonias*. These are readily soluble in water but not in ether, hence ammonia gas will precipitate them in crystalline form from the ethereal solution of the aldehydes. They are rather unstable, and dilute acids again resolve them into their components. Pyridine bases are produced when the aldehyde-ammonias are heated.

(*b*) Aldehydes and primary amines combine, with the exit of water, to form *aldehyde-imides* (p. 161).

(*c*) By an exit of water the aldehydes unite with *hydroxylamine* to form the so-called *aldoximes* (V. Meyer, B. **15**, 2778).

It is very evident that at first, in these cases, there is formed an unstable intermediate product (compare chloral hydroxylamine, p. 206) corresponding to aldehyde-ammonia:



$$CH_3C\genfrac{}{}{0pt}{}{\diagup\!\!\diagup O}{\diagdown H} \xrightarrow{NH_2OH} \left(CH_3 . C\genfrac{}{}{0pt}{}{\diagup NHOH}{\genfrac{}{}{0pt}{}{-OH}{\diagdown H}}\right) \xrightarrow{-H_2O} CH_3 . CH : NOH.$$

(*d*) The aldehydes deport themselves similarly with *phenylhydrazine;* water separates and *hydrazones* (E. Fischer) result:

$$CH_3 . CHO + H_2N . HN . C_6H_5 = CH_3 . CH : N . NH . C_6H_5 + H_2O.$$

These serve admirably for the detection and characterization of the aldehydes. The aldoximes and hydrazones, when boiled with acids, absorb water and revert to their parent substances. They yield primary amines when reduced (p. 161).

(*e*) The aldehydes also unite with p-amido-dimethyl aniline (B. **17**, 2939), with the amido-phenols and other aromatic bases (Schiff, B. **25**, 2020).

(9) Compounds are formed by the action of phosphorus trichloride upon aldehydes, which are converted by water into *oxyalkyl-phosphinic acids*, *e. g.*, $CH_3 . CH(OH)\text{-}PO(OH)_2$ (B. **18**, R. 111).

(10) Phosphorus pentachloride and phosphorus trichlor-dibromide replace the aldehyde oxygen by chlorine or bromine and yield dichlorides and dibromides, in which the two halogen atoms are linked to a terminal carbon atom (p. 102):

$$CH_3 . CHO + PCl_5 = CH_3CHCl_2 + POCl_3.$$

(11) The hydrogen atoms of the alkyl groups of the aldehydes may be replaced by chlorine and bromine, as well as by iodine and iodic acid.

(12) The lower members of the homologous series of the aldehydes

polymerize very readily. The *polymerization* of the aldehydes and thioaldehydes depends upon the union of several aldehyde radicals, $CH_3.-CH=$, through the oxygen or sulphur atoms (A. **203**, 44). This phenomenon will be fully treated under formaldehyde and acetaldehyde (p. 194).

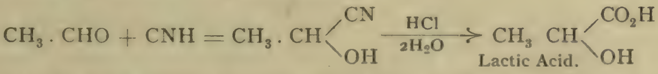
B. *Nucleus synthetic Reactions of the Aldehydes.* (1) *Aldol Condensations.*—Two (or more) aldehyde molecules may unite, under proper conditions, by means of carbon linkings. Thus, aldehyde alcohols are formed from acetaldehyde: *Aldol* (Würtz) or *β*-oxybutyraldehyde, $CH_3 . CHOH . CH_2 . CHO$ (see this).

Similarly, aldehyde or chloral and acetone (p. 213), aldehyde and malonic ester, unite with one another. But almost invariably the resulting oxy-derivatives split off water and pass into unsaturated bodies: aldol into *crotonaldehyde*, $CH_3CH = CH . CHO$.

These are nucleus-syntheses and are often termed **condensation reactions.** The reagents suitable for the production of such reactions are mineral acids, zinc chloride, caustic alkalies, a sodium acetate solution, etc. Condensation reactions, in which an aliphatic aldehyde plays the rôle of one of the component or parent substances, will be frequently encountered. A reaction discovered by Perkin, Sr., when working with aromatic aldehydes, has been employed quite frequently to unite aldehydes and acetic acid, as well as mono-alkyl acetic acids, in such a manner that the products are unsaturated monocarboxylic acids (see *nonylenic acid*). The aldehydes unite in like manner with succinic acid, forming *γ*-lactone carboxylic acids—the *paraconic acids* (see these).

(2) Aldehydes can also unite with zinc alkyls. This union is accompanied by the breaking down of the double union between carbon and oxygen. The action of water on the addition product produces a secondary alcohol (p. 114). Olefine alcohols result by the use of allyl iodide and zinc (p. 131).

(3*a*) Aldehydes also combine with hydrogen cyanide, yielding *oxycyanides* or cyanhydrins—the *nitriles* of *α oxy-acids* (see these), which will be discussed after the *α-oxy-acids*, and which can be obtained from them by means of hydrochloric acid:



$$CH_3 . CHO + CNH = CH_3 . CH{<}^{CN}_{OH} \xrightarrow[2H_2O]{HCl} \underset{\text{Lactic Acid.}}{CH_3\ CH}{<}^{CO_2H}_{OH}$$

(*b*) Aldehydes and ammonium cyanide combine; water separates, and the *nitriles of α-amido-acids, e g.*, $CH_3 . CH{<}^{NH_2}_{CN}$, result. When treated with hydrochloric acid they yield amido-acids (see these). The same *amido-nitriles* are produced by the action of CNH upon the aldehyde ammonias, and from the oxy-cyanides and ammonia. Cyanides of *α-anilido-* and *α-phenyl hydrazido-acids* are formed by the addition of prussic acid to the *aliphatic aldehyde-anilines* and *aldehydephenylhydrazones* (B. **25**, 2020).

Formic Aldehyde, *Methyl Aldehyde* [Methanal] $H.C{<}^{O}_{H}$, was discovered by A. W. Hofmann, and was until recently only known in aqueous solution and in vapor form. It may, as was shown by Kekulé, be condensed by strong cooling to a colorless liquid, boiling at —21°, and having at —80° the sp. gr. 0.9172; at —20°, the sp. gr. 0.8153.

Liquid formaldehyde changes slowly at —20°, rapidly at the ordinary temperature, with a snapping noise, into *trioxymethylene* $(CH_2O)_3$ (B. **25**, 2435). This polymeric modification was known before the simple formaldehyde. It resolves itself into the latter on the application of heat. Formaldehyde possesses a sharp, penetrating odor, and destroys bacteria of the most varied sort. It is applied under the name of *formaline*, either in solution or as a gas, for disinfecting purposes (B. **27**, R. 757, 803; **28**, R. 938; **29**, R. 178, 288, 426).

Methods of Formation.—(1) It is produced if the vapors of methyl alcohol, mixed with air, are conducted over an ignited platinum spiral or ignited copper gauze (J. pr. Ch. **33**, 321; B. **19**, 2133; **20**, 144; A. **243**, 335). Lamps have been constructed for the production of formaldehyde. Methyl alcohol is oxidized in them in the presence of a platinum wire gauze. Compare B. **28**, 261. (2) When chlorine and bromine act upon methyl alcohol, formic aldehyde is produced (B. **26**, 268), and is converted by them in sunlight into haloid acids and carbon dioxide (B. **29**, R. 88). (3) It also arises in small quantity in the distillation of *calcium formate*. (4) By the digestion of *methylal*, $CH_2(OCH_3)_2$ (p. 200) with sulphuric acid (B. **19**, 1841).

Mercklin and Lösekann, in Seelze, near Hannover, manufacture formaldehyde technically from methyl alcohol by a method not well known, and offer its 40 per cent. solution to trade, together with numerous other derivatives of formaldehyde. The quantity of formic aldehyde is determined by its conversion into hexamethyleneamine, $(CH_2)_6N_4$ (B. **16**, 1333; **22**, 1565, 1929; **26**, R. 415). In the presence of lime formaldehyde condenses to *a-acrose* or (d + l) fructose (see this). It yields *pentaerythrite* $C(CH_2OH)_4$ (see this) (B. **26**, R. 713) with acetaldehyde. Formic aldehyde condenses in like manner with ketone-like bodies.

In the various reactions of formaldehyde its oxygen unites with two hydrogen atoms of the reacting body to yield water. It is immaterial whether the hydrogen is in union with carbon, nitrogen, or oxygen. The products are diphenylmethane derivatives, methylene aniline, and formals of polyhydric alcohols (A. **289**, 20).

Polymeric Modifications of Formaldehyde.—The concentrated aqueous solution of formic acid not only contains volatile CH_2O, but also the hydrate $CH_2<\begin{smallmatrix}OH\\OH\end{smallmatrix}$, *i. e.*, hypothetical methylene glycol, and non-volatile polyhydrates, *e. g.*, $(CH_2)_2O(OH)_2$, corresponding to polyethylene glycols. Therefore the determinations of the molecular weight of the solution, by the method of Raoult, have yielded different values (B. **21**, 3503; **22**, 472). On complete evaporation of the solution the hydrates condense to the solid anhydride $(CH_2O)_n$, paraformaldehyde, possibly *diformaldehyde*, $(CH_2O)_2$.

Trioxymethylene, $(CH_2O)_3$, or Metaformaldehyde, is distinguished from the so-called paraformaldehyde, whose simplicity has not yet been established, by its insolubility in water, alcohol, and ether. It is obtained by the action of silver oxide upon methene di-iodide, or by heating methene di-acetyl ester with water, to 100°; by distilling glycollic acid with a little concentrated sulphuric acid, and by the concentration of formic aldehyde (see above). It is a white, indistinctly crystalline mass. It melts at 171°. The vapors have the formula CH_2O, which corresponds to their density. When cooled they again condense to the trimolecular form. When it is heated with water to 130° it changes to the simple molecule CH_2O, but by prolonged heating carbon dioxide and methyl alcohol are produced (B. **29**, R. 688).

When dry trioxymethylene is heated with a trace of sulphuric acid to 115° in a sealed tube it is changed into the isomeric *Trioxymethylene*, $(CH_2O)_3$, crystallizing in long needles and melting at 60–61° (B. **17**, R. 567).

The polymeric modifications of formaldehyde have not yet been as successfully studied as the polymeric acetaldehydes.

Acetaldehyde, $C_2H_4O = CH_3.CHO$, *Ethylidene Oxide* [Ethanal], is formed according to the usual methods: (1) From ethyl alcohol; (2) from calcium acetate; (3) from acetyl chloride or acetic anhydride; (4) from ethylidene chloride; (5) from acetal and ethidene diacetate; (6) from lactic acid, and (7) from sodium nitroethane. It occurs in the first runnings in the rectification of spirit, and is made, too, in the oxidation of alcohol in running over wood charcoal (p. 123).

History.—In 1774 Scheele noticed that aldehyde was formed when alcohol was oxidized with manganese dioxide and sulphuric acid. Döbereiner, however, was the first person to isolate the aldehyde in the form of aldehyde-ammonia, which he gave for investigation to Liebig, who then established the composition of aldehyde and showed its relation to alcohol. It was Liebig who introduced the name *Al*(cohol) *dehyd*(e)(rogenatus) into chemical science (A. **14**, 133; **22**, 273; **25**, 17). Ordinary aldehyde readily polymerizes to liquid *paraldehyde*, and solid *metaldehyde*. Fehling first observed the former, and Liebig the latter. Kekulé and Zincke determined the conditions of formation for the aldehyde modifications and cleared up the somewhat confused reaction relations (A. **162**, 125).

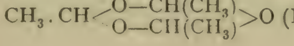
Preparation.—Pour 12 parts H_2O over 3 parts $K_2Cr_2O_7$ (B. **27**, R. 471), and then gradually add, taking care to have the solution cooled, a mixture of 4 parts concentrated H_2SO_4 and 3 parts alcohol (90 per cent.). The escaping aldehyde vapors are conducted into ether, and this solution saturated with dry NH_3, when the aldehyde-ammonia will separate in a crystalline form. Pure aldehyde may be obtained from this by distilling it together with dilute sulphuric acid. The aldehyde vapors are freed from moisture by conducting them over dehydrated calcium chloride.

Acetaldehyde is a mobile, peculiar-smelling liquid. It boils at 20.8°, and has a sp. gr. of 0.8009 at 0°. It is miscible in all proportions with water, ether and alcohol. It is prepared technically in order to obtain *paraldehyde* and *quinaldine* (see this).

Polymeric Aldehydes.—Small quantities of acids (HCl, SO_2) or salts (especially $ZnCl_2$, CH_3CO_2Na) convert aldehyde at *ordinary temperatures* into **paraldehyde,** $(C_2H_4O)_3$; the change (accomplished by evolution of heat and contraction) is particularly rapid, if a few drops of sulphuric acid be added to the aldehyde. Paraldehyde is a colorless liquid boiling at 124°, and of sp. gr. 0.9943 at 20°. It dissolves in about 12 vols. H_2O, and is, indeed, more soluble in the cold than in the warm liquid. This behavior would point to the formation of a hydrate. The vapor density agrees with the formula $C_6H_{12}O_3$. Paraldehyde is applied in medicine as a sleep-producer. When distilled with sulphuric acid ordinary aldehyde is generated.

Metaldehyde, $(C_2H_4O)_n$, is produced by the same reagents (see above) acting on ordinary aldehyde *at temperatures below* 0°. It is a white crystalline body, insoluble in water, but readily dissolved by hot alcohol and ether. If heated to 112°–115° it sublimes without previously melting, and passes into ordinary aldehyde with only slight decomposition. When heated in a sealed tube the change is complete. Exposed for several days to a temperature varying from 60°–65°, metaldehyde passes into aldehyde and paraldehyde (B. **26**, R. 775).

The vapor density and the lowering of the freezing point, in a phenol solution, indicate that the two aldehyde modifications possess the formula $(C_2H_4O)_3$ (B. **27**, R. 306). Chemical behavior, refractive power (p. 65), and specific volume favor the single linkage of oxygen and carbon; that, therefore, the three oxygen atoms unite the three ethylidene groups to a ring of six members:



$$\mathrm{CH_3.CH}{<}\begin{matrix}\mathrm{O-CH(CH_3)}\\ \mathrm{O-CH(CH_3)}\end{matrix}{>}\mathrm{O}$$

(B. **24**, 650; **25**, 3316; **26**, R. 185).

They may be considered cyclic ethers of ethidene glycol, whose anhydride is acetaldehyde. Paraldehyde and metaldehyde appear to be structurally identical. Compare the polymeric *thialdehydes* (p. 202) for the possibility of explaining their differences by stereochemical relations.

Behavior of Acetaldehyde (*Paraldehyde* and *Metaldehyde*). (1) In the air acetaldehyde slowly oxidizes to acetic acid. It throws out a silver mirror from an ammoniacal silver nitrate solution. Paraldehyde and metaldehyde do not reduce silver solutions. (2) Alkalies convert acetaldehyde into *aldehyde resin*. (3) It is changed to *ethyl alcohol* by nascent hydrogen. (4) Aldehyde unites with alcohol to form *acetal* (p. 200). (5) Hydrogen sulphide converts it into *thioaldehyde* (p. 202), and with *mercaptans* it forms *mercaptals* (p. 202). (6) Acetic anhydride changes it to *ethidene diacetate* (p. 202). (7) On shaking aldehyde with a very concentrated solution of an alkaline bisulphite crystalline compounds separate, *e. g.*, *potassium oxyethidene sulphonate*, $CH_3 . CH(OH)SO_3K$, which are resolved into their components when treated with acids (p. 204):

$$CH_3 . CHO + SO_3HK = CH_3 . CH < \genfrac{}{}{0pt}{}{SO_3K}{OH}$$

$$CH_3 . CH < \genfrac{}{}{0pt}{}{SO_3K}{OH} + HCl = CH_3 . CHO + SO_2 + H_2O + KCl.$$

Paraldehyde and metaldehyde do not unite with the bisulphites of the alkalies. (8) Acetaldehyde reacts with ammonia, hydroxylamine, and phenylhydrazine, while paraldehyde and metaldehyde fail to do so. (9) Phosphorus pentachloride converts acetaldehyde, paraldehyde and metaldehyde into ethidene chloride (p. 201).

For the *condensation* of aldehyde to *aldol*, *crotonaldehyde* and other compounds see p. 193.

Aldehyde combines with hydrocyanic acid, the product being the nitrile of the lactic acid of fermentation, which may be synthesized in this manner.

The **homologues of formic and acetaldehydes** are prepared either (1) by the oxidation of the corresponding primary alcohols, or (2) by the distillation of the calcium or barium salts of the corresponding fatty acids, mixed with calcium or barium formate:

Name.	Formula.	Boiling Point.	M. P.
Propyl Aldehyde [Propanal], ...	$CH_3 . CH_2 . CHO$	—	49°
n-Butyraldehyde [Butanal], ...	$(CH_3) . (CH_2)_2 . CHO$	—	75°
Isobutyraldehyde [Methyl Propanal], .	$(CH_3)_2CH . CHO$	—	61°
n-Valeraldehyde [Pentanal], ...	$(CH_3)(CH_2)_3CHO$	—	103°
Isovaleraldehyde [2-Methylbutanal (4)],	C_4H_9CHO	—	92°
Methyl-ethyl Acetaldehyde, ...	C_4H_9CHO	—	91°
Trimethyl Acetaldehyde (B. **24**, R. 898),	$(CH_3)_3C . CHO$	—	74°
n-Capric Aldehyde, ...	$CH_3 . [CH_2]_4CHO$	—	128°
Methyl-n-propyl Acetaldehyde, ...	$C_5H_{11}CHO$	—	116°
Isobutyl Acetaldehyde, ...	$C_5H_{11}CHO$	—	121°
Œnanthyl Aldehyde, Œnanthol,	$CH_3[CH_2]_5CHO$	—	155°
Capric Aldehyde, $C_{10}H_{20}O$, ...	$CH_3[CH_2]_8CHO$	—	(106°)
Lauric Aldehyde, $C_{12}H_{24}O$, ...	$CH_3[CH_2]_{10}CHO$	44.5°	(142°)
Myristic Aldehyde, $C_{14}H_{28}O$, ...	$CH_3[CH_2]_{12}CHO$	52.5°	(168°)
Palmitic Aldehyde, $C_{16}H_{32}O$, ...	$CH_3[CH_2]_{14}CHO$	58.5°	(192°)
Stearic Aldehyde, $C_{18}H_{34}O$, ...	$CH_3[CH_2]_{16}CHO$	63.5°	(212°)

The enclosed boiling points were determined under diminished pressure. In the case of capric aldehyde the pressure was 15 mm.; with all the rest it was 22 mm.

Propyl aldehyde, by the action of hydrochloric acid, yields both **parapropyl aldehyde**, boiling at 169°, and **metapropyl aldehyde**, melting at 180°. They have the molecular formula $(C_3H_6O)_3$ (B. **28**, R. 469).

Œnanthylic Aldehyde, Œnanthol (*οἶνος*, wine), is very readily prepared. It is formed together with undecylenic acid when the acid of *castor oil* is distilled under diminished pressure:

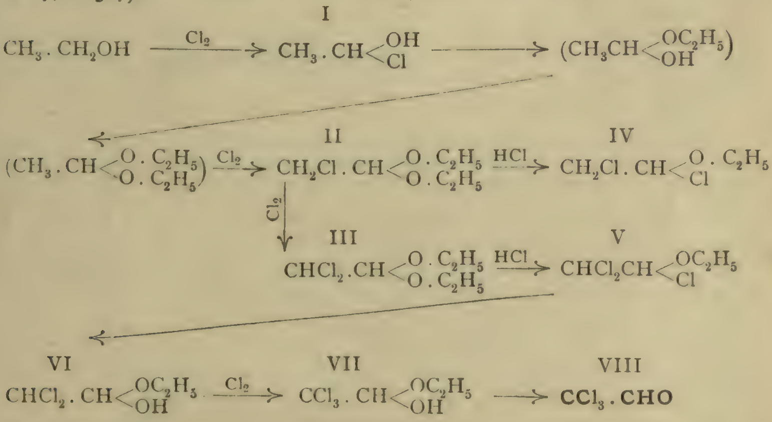
$$\underset{\substack{\text{Ricinoleic}\\\text{Acid}}}{C_{18}H_{34}O_3} = \underset{\substack{\text{Undecylenic}\\\text{Acid}}}{C_{10}H_{19}.CO_2H} + \underset{\text{Œnanthol.}}{CH_3.[CH_2]_5CHO.}$$

1. HALOGEN SUBSTITUTION PRODUCTS OF THE LIMIT ALDEHYDES.

Chloral, Trichloracetaldehyde, is the most important halogen substitution product of aldehyde. For this reason it will receive first attention.

Trichloracetaldehyde, Chloral, $CCl_3.CHO$, was discovered in 1832 by Liebig while engaged in studying the action of chlorine upon alcohol (A. **1**, 182).

Fritsch considers that chlorine acts upon alcohol to produce at first monochloralcohol or aldehyde chlorhydrin (I). Alcohol and hydrochloric acid convert this, through the aldehyde alcoholate, into acetal. Obviously acetal is chlorinated too easily to mono- and dichloracetal (II and III). These two compounds, under the influence of hydrochloric acid, pass into dichlor- and trichlor-ether (IV and V). Water changes the latter to dichloracetaldehyde alcoholate (VI), which is converted by chlorine into chloral alcoholate. Sulphuric acid decomposes the latter into alcohol and chloral (VIII) (A. **279**, 288; compare also the chlorination of isobutyl alcohol, B. **27**, R. 507).



$$\mathrm{CH_3.CH_2OH} \xrightarrow{Cl_2} \overset{\mathrm{I}}{\mathrm{CH_3.CH}{<}\begin{smallmatrix}\mathrm{OH}\\ \mathrm{Cl}\end{smallmatrix}} \longrightarrow \left(\mathrm{CH_3CH}{<}\begin{smallmatrix}\mathrm{OC_2H_5}\\ \mathrm{OH}\end{smallmatrix}\right)$$

$$\left(\mathrm{CH_3.CH}{<}\begin{smallmatrix}\mathrm{O.C_2H_5}\\ \mathrm{O.C_2H_5}\end{smallmatrix}\right) \xrightarrow{Cl_2} \overset{\mathrm{II}}{\mathrm{CH_2Cl.CH}{<}\begin{smallmatrix}\mathrm{O.C_2H_5}\\ \mathrm{O.C_2H_5}\end{smallmatrix}} \xrightarrow{HCl} \overset{\mathrm{IV}}{\mathrm{CH_2Cl.CH}{<}\begin{smallmatrix}\mathrm{O.C_2H_5}\\ \mathrm{Cl}\end{smallmatrix}}$$

$$\downarrow Cl_2$$

$$\overset{\mathrm{III}}{\mathrm{CHCl_2.CH}{<}\begin{smallmatrix}\mathrm{O.C_2H_5}\\ \mathrm{O.C_2H_5}\end{smallmatrix}} \xrightarrow{HCl} \overset{\mathrm{V}}{\mathrm{CHCl_2CH}{<}\begin{smallmatrix}\mathrm{OC_2H_5}\\ \mathrm{Cl}\end{smallmatrix}}$$

$$\overset{\mathrm{VI}}{\mathrm{CHCl_2.CH}{<}\begin{smallmatrix}\mathrm{OC_2H_5}\\ \mathrm{OH}\end{smallmatrix}} \xrightarrow{Cl_2} \overset{\mathrm{VII}}{\mathrm{CCl_3.CH}{<}\begin{smallmatrix}\mathrm{OC_2H_5}\\ \mathrm{OH}\end{smallmatrix}} \longrightarrow \overset{\mathrm{VIII}}{\mathbf{CCl_3.CHO}}$$

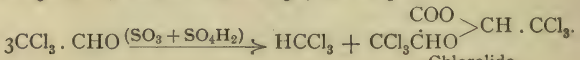
Chloral hydrate, *dichloracetic ester*, *trichlor-ethyl alcohol* (B. **26**, 2756), and *ethylene monochlorhydrin* are by-products in the manufacture of chloral. (Private communication from Anschütz and Stiepel.)

Chloral is an oily, pungent-smelling liquid, which boils at 97° and has the sp. gr. 1.541 at 0°. When kept for some time it passes into a solid polymeride.

Chloral shows greater tendency than acetaldehyde to sever its double linkage, between carbon and oxygen, and to enter addition-reactions. Like acetaldehyde it not only combines with acetic anhydride, the alkaline bisulphites, ammonia and hydrocyanic acid, but also with water, alcohol, hydroxylamine, formamide—four substances with which acetaldehyde is incapable of uniting.

The following reactions of chloral should also be observed: (1) The alkalies break it down into *chloroform* and alkali formates; (2) fuming sulphuric acid condenses it to *chloralide* (see this), trichlorlactic-trichlorethidene ether ester; (3) potassium cyanide changes it to dichloracetic ethyl ester (see this):

(1) $CCl_3CHO + KOH = HC.Cl_3 + H.CO_2K$

(2) 

$$3CCl_3.CHO \xrightarrow{(SO_3+SO_4H_2)} HCCl_3 + \begin{matrix} COO \\ CCl_3\dot{C}HO \end{matrix}\!\!>CH.CCl_3.$$

Chloralide.

Chloral Hydrate, *Trichlorethidene Glycol,* $CCl_3.CH{<}\begin{smallmatrix}OH\\OH\end{smallmatrix}$, results from the union of chloral with water. It is technically prepared on a very large scale. It consists of large monoclinic prisms, fusing at 57° and distilling at 96–98°. The vapors dissociate into chloral and water. Chloral hydrate dissolves readily in water, possesses a peculiar odor and a sharp, biting taste; when taken internally it produces sleep, which fact was discovered in 1869 by Liebreich (B. **2**, 269). It occurs in urine as urochloralic acid (see this). Concentrated sulphuric acid resolves the hydrate into water and chloral. It reduces ammoniacal silver solutions and when oxidized with nitric acid yields *trichloracetic acid.*

In chloral hydrate we encounter the first example of a body which, contrary to the rule, contains two hydroxyl groups attached to the same carbon atom, without having the immediate spontaneous exit of water.

Chloral Alcoholate, $CCl_3.CH{<}\begin{smallmatrix}OC_2H_5\\OH\end{smallmatrix}$, melting at 65° and boiling at 114–115°, is the chief product in the action of chlorine upon alcohol (p. 197). It is also produced when chloral and chloral hydrate are treated with alcohol. When brought in contact with water it gradually reverts to chloral hydrate (B. **28**, R. 1013).

Chloral Ethyl Acetate, $CCl_3.CH{<}\begin{smallmatrix}O.C_2H_5\\O.COCH_3\end{smallmatrix}$, boiling at 198°, is obtained by the action of acetyl chloride on the alcoholate.

Other Halogen Substitution Products of Acetaldehyde.—Dichloracetaldehyde, boiling at 88–90°, results from the action of concentrated H_2SO_4 upon *dichloracetal,* $CHCl_2.CH(OC_2H_5)_2$. *Dichloracetaldehyde Hydrate,* $CHCl_2.CH(OH)_2$, melts at 57° and boils at 120°. *Monochloracetaldehyde* boils at 85°. It is formed when *monochloracetal* (p. 200) is distilled with anhydrous oxalic acid. It polymerizes very readily (B. **15**, 2245).

Tribromaldehyde, Bromal, $CBr_3.CHO$, is perfectly analogous to chloral. It boils at 172–173°. Heated with alkalies bromal breaks up into bromoform, $CHBr_3$, and a formate. The **alcoholate** melts at 44° and decomposes at 100°.

Bromal Hydrate, Tribromethidene Glycol, $CBr_3CH(OH)_2$, melts at 53°.

Bromal Alcoholate, $CBr_3CH(OH)(O.C_2H_5)$, melts at 44°.

Dibromacetaldehyde, obtained by the bromination of paraldehyde, boils at 142°.

Bromacetaldehyde boils between 80° and 105°, and is produced, like monochloracetaldehyde, from *monobromacetal.*

Iodo-acetaldehyde, $CH_2I.CHO$, is made by acting on aldehyde with iodine or iodic acid. It is an oily liquid, which decomposes at 80° (B. **22**, R. 561).

The relations of the three chlor- (or brom-) acetaldehydes to the oxygen derivatives, whose chlorides they may be considered, are manifest in the following arrangement (p. 193):

$CH_2Cl.CHO$, Chloracetaldehyde	$CH_2(OH).CHO$, Glycolylaldehyde
$CHCl_2.CHO$, Dichloracetaldehyde	$CHO.CHO$, Glyoxal
$CCl_3.CHO$, Trichloracetaldehyde	$CO_2H.CHO$, Glyoxylic acid.

Higher Chlorine Substitution Products of the Aldehydes:

β-**Chlorpropionic Aldehyde,** $CH_2Cl.CH_2.CHO$, from *acrolein*, $CH_2 = CH.CHO$, and hydrochloric acid, melts at 35°.

β-**Chlorbutyraldehyde,** $CH_3.CHCl.CH_2.CHO$, is produced from crotonaldehyde, $CH_3.CH:CH.CHO$, by the addition of HCl, and fuses at 96°. Nitric acid oxidizes it to β-chlorbutyric acid.

$\alpha\alpha\beta$-**Trichlorbutyraldehyde,** $CH_3.CHCl.CCl_2.CHO$, *butylchloral*, boils at 163–165° (compare acetamide).

Butylchloral Hydrate, $CH_3CHCl.CCl_2.CH(OH)_2$, melts at 78°, and is formed from α-chlorcrotonaldehyde and Cl_2. Alkalies decompose it into *formic acid*, potassium chloride, and *dichlorpropylene*, $CH_3.CCl:CHCl$. When taken into the system it appears in the urine as *urobutyrchloralic acid* (see this), and is converted, by nitric acid, into trichlorbutyric acid.

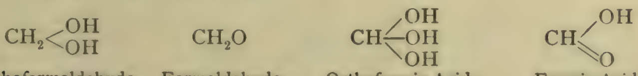
The relations of these three chlorinated aldehydes to the unsaturated aldehydes, from which they are formed by the addition of HCl or Cl_2, and to the acids which they yield on oxidation, are shown in the following table:

$$\begin{array}{ccccc}
\underset{\text{Acroleïn}}{CH_2=CH.CHO} & \xrightarrow{HCl} & \underset{\beta\text{-Chlorpropionic Aldehyde}}{CH_2Cl.CH_2.CHO} & \xrightarrow{NO_3H} & \underset{\beta\text{-Chlorpropionic Acid}}{\overset{\beta}{C}H_2Cl.\overset{\alpha}{C}H_2.CO_2H} \\
\underset{\text{Crotonaldehyde}}{CH_3.CH=CH.CHO} & \xrightarrow{HCl} & \underset{\beta\text{-Chlorbutyraldehyde}}{CH_3.CHCl.CH_2CHO} & \longrightarrow & \underset{\beta\text{-Chlorbutyric Acid}}{CH_3.CHCl.CH_2.CO_2H} \\
\underset{\alpha\text{-Chlorcrotonaldehyde}}{CH_3.CH=CCl.CHO} & \xrightarrow{Cl_2} & \underset{\text{Butylchloral}}{CH_3.CHCl.CCl_2.CHO} & \longrightarrow & \underset{\text{Trichlorbutyric Acid.}}{CH_3.CHCl.CCl_2.CO_2H}
\end{array}$$

2. ETHERS AND ESTERS OF METHYLENE AND ETHIDENE GLYCOLS.

In the introduction to the aldehydes (p. 188) it was explained that these bodies could be regarded as *anhydrides* (see chloral hydrate, p. 198) of *glycols*, only capable of existing in exceptional cases. In the latter the two hydroxyl groups were linked to the same terminal carbon atom. Stable ethers and esters of these hypothetical glycols are, however, known.

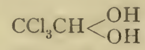
These hypothetical glycols might also be designated orthoaldehydes, because they bear the same relation to the aldehydes that the hypothetical orthocarbonic acids sustain to the carboxylic acids:



$$CH_2{<}^{OH}_{OH} \qquad CH_2O \qquad CH{\equiv}(OH)_3 \qquad CH{\lessgtr}^{OH}_{O}$$

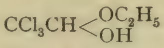
Orthoformaldehyde Formaldehyde Orthoformic Acid Formic Acid.

Basic and neutral mono- and dialkyl-ethers may be obtained from a dihydric alcohol. The only mono-ether to be noticed in this connection is *chloral alcoholate*, which was mentioned under chloral hydrate:



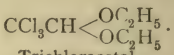
$$CCl_3CH<\substack{OH\\OH}$$

Chloral Hydrate



$$CCl_3CH<\substack{OC_2H_5\\OH}$$

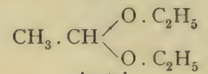
Chloral Alcoholate



$$CCl_3CH<\substack{OC_2H_5\\OC_2H_5}.$$

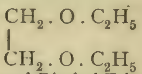
Trichloracetal.

Alcohols not highly substituted by halogens are as little able to combine with a molecule of alcohol as with water. The dialkyl ethers are named *acetals*, from their best-known representative. They are isomeric with the ethers of the corresponding *true glycols*, whose OH-groups are attached to different carbon atoms:



$$CH_3.CH<\substack{O.C_2H_5\\O.C_2H_5}$$

Acetal



$$\begin{array}{l}CH_2.O.C_2H_5\\ |\\ CH_2.O.C_2H_5\end{array}$$

Glycol Diethyl Ether.

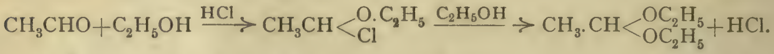
The polymeric aldehyde modifications, described under the aldehydes, should also be viewed as ether-like derivatives of the glycols, the anhydrides of which are the aldehydes.

A. **Acetals** are produced (1) when alcohols are oxidized with MnO_2 and H_2SO_4. The aldehyde formed at first unites with alcohol with the simultaneous separation of water:

$$3CH_3.CH_2OH \xrightarrow{O} CH_3CH(O.C_2H_5)_2 + 2H_2O.$$

(2) When aldehydes are heated with the alcohols alone to 100°; and from trioxymethylene and alcohols on the addition of ferric chloride (1–4 per cent.) (B. **27**, R. 506).

(3) By the action of gaseous HCl upon a mixture of alcohol and aldehyde, *chlorhydrin* (see ethylene glycol) being the first product:



$$CH_3CHO+C_2H_5OH \xrightarrow{HCl} CH_3CH<\substack{O.C_2H_5\\Cl} \xrightarrow{C_2H_5OH} CH_3.CH<\substack{OC_2H_5\\OC_2H_5}+HCl.$$

(4) By the action of alcoholates upon the corresponding chlorides, bromides and iodides.

On heating the acetals with alcohols, the higher alkyls are replaced by the lower (A. **225**, 265). When the acetals are digested with aqueous hydrogen chloride they are resolved into their constituents. They dissolve readily in alcohol and in ether, but with difficulty in water.

Methylal, Methylene-dimethyl Ether, Formal, $CH_2(OCH_3)_2$, boils at 42° and has the sp. gr. 0.855. It is an excellent solvent for many carbon compounds. **Methylene-dimethyl Ether,** $CH_2(OC_2H_5)_2$, boils at 89°. For the higher *methylals* see B. **20**, R. 553; **27**, R. 507.

Ethidene-dimethyl Ether, Dimethyl Acetal, $CH_3CH(OCH_3)_2$, boils at 64°. *Acetal, ethidene-diethyl ether*, $CH_3CH(OC_2H_5)_2$, boils at 104°. Its sp. gr. is 0.8314 at 20°. It is produced in the process of brandy distillation. It is quite stable towards the alkalies, while dilute acids readily break it down into aldehyde and alcohol (B. **16**, 512).

Chlorine acting upon acetal produces—

(1) **Monochloracetal,** $CH_2Cl.CH(O.C_2H_5)_2$, boiling at 157° (B. **24**, 161). It also results from *Dichlor-ether*, $CH_2Cl.CHCl.OC_2H_5$, and alcohol or sodium ethylate (B. **21**, 617).

(2) **Dichloracetal,** $CHCl_2.CH(O.C_2H_5)_2$, boiling at 183–184°.

Alcohol and chlorine yield—

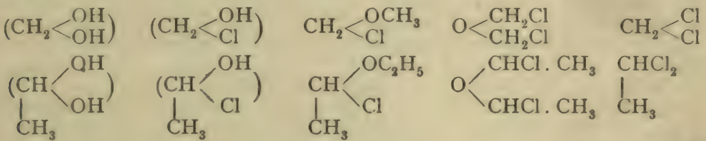
Trichloracetal, $CCl_3.CH(OC_2H_5)_2$, boiling at 197°.

Monobromacetal, $CH_2BrCH(OC_2H_5)_2$, boiling at 170°, is produced from acetal, bromine and $CaCO_3$ (B. **25**, 2551). Sulphuric acid decomposes the chlorinated acetals into alcohol and *chlorinated aldehydes* (p. 198).

B. Dihalogen Aldehydes and Aldehyde Halohydrins, their Alkyl Ethers and Anhydrides.

In describing the dihalogen substitution products of the paraffins it was indicated that compounds in which two halogen atoms occur joined to the same terminal carbon atom bear an intimate genetic relation to the aldehydes, and are therefore called aldehyde dihaloids.

If these compounds be referred to the glycols containing two hydroxyl groups attached to the same terminal carbon atom,—*i.e.*, the hypothetical ortho-aldehydes,—then the aldehyde haloids are the neutral haloid esters of these glycols. Between the ortho-aldehydes and the aldehyde haloids stand the monohaloid esters, the aldehyde halohydrins, isomeric with the monohaloid esters of the true glycols,—the glycol halohydrins,—but only known in the form of their alkyl ethers, the α-monohaloids, ordinary ethers and their anhydrides, the symmetrical α-disubstituted, ordinary ethers:



$$\left(CH_2<\begin{smallmatrix}OH\\OH\end{smallmatrix}\right)\quad \left(CH_2<\begin{smallmatrix}OH\\Cl\end{smallmatrix}\right)\quad CH_2<\begin{smallmatrix}OCH_3\\Cl\end{smallmatrix}\quad O<\begin{smallmatrix}CH_2Cl\\CH_2Cl\end{smallmatrix}\quad CH_2<\begin{smallmatrix}Cl\\Cl\end{smallmatrix}$$

$$\left(\begin{matrix}CH<\begin{smallmatrix}OH\\OH\end{smallmatrix}\\|\\CH_3\end{matrix}\right)\quad \left(\begin{matrix}CH<\begin{smallmatrix}OH\\Cl\end{smallmatrix}\\|\\CH_3\end{matrix}\right)\quad \begin{matrix}CH<\begin{smallmatrix}OC_2H_5\\Cl\end{smallmatrix}\\|\\CH_3\end{matrix}\quad O<\begin{smallmatrix}CHCl.CH_3\\CHCl.CH_3\end{smallmatrix}\quad \begin{matrix}CHCl_2\\|\\CH_3\end{matrix}$$

The genetic relations of the aldehyde haloids to the aldehydes consist in the formation of aldehyde chlorides from the aldehydes by means of PCl_5, and the transposition of the aldehyde chlorides when heated to 100° with water.

1. **Aldehyde Dihaloids.**—The boiling points, melting points and specific gravities of some of the simple aldehyde dihaloids are given in the appended table. The inclosed numbers after the boiling points indicate diminished pressure:

Name.	Formula.	M. P.	B. P.	Sp. Gr.
Methylene Chloride, . .	CH_2Cl_2	—	41°	1.37 (0°)
Methylene Bromide, . .	CH_2Br_2	—	98°	2.54 (0°)
Methylene Iodide, . . .	CH_2I_2	+ 4°	150° (330)	3.28 (15°)
Ethidene Chloride, . . .	CH_3CHCl_2	—	58°	1.17 (20°)
Ethidene Bromide, . . .	CH_3CHBr_2	—	110°	2.02 (20°)
Ethidene Iodide, ...	CH_3CHI_2	—	127° (171)	2.84 (0°)
Propidene Chloride, . .	$CH_3.CH_2CHCl_2$	—	86°	1.16 (14°)

Methylene Chloride is formed from CH_3Cl and Cl, and by the reduction of chloroform by means of zinc in alcohol.

Methylene Bromide results on heating CH_3Br with bromine to 180°, and by the action of trioxymethylene upon aluminium bromide.

Methylene Iodide is produced when iodoform is reduced with HI, or better, with arsenious acid and sodium hydroxide (Klinger). It is characterized by a high specific gravity; chlorine and bromine change it to methylene chloride and bromide (compare ethylene, p. 90).

Ethidene Chloride, *Aldehyde Chloride*, is produced (1) from aldehyde by the action of PCl_5, (2) from vinyl bromide by means of hydrogen bromide, and (3) by treating copper acetylide with concentrated hydrochloric acid (A. 178, 111) (compare ethylene, p. 90).

Ethidene Bromide is obtained by the action of PCl_3Br_2 upon aldehyde (B. 5, 289).

Ethidene Iodide is obtained from acetylene and hydrogen iodide (B. 28, R. 1014).

2. **Alkyl Ethers of the Aldehyd Halohydrins, *a*-Monohaloid Ethers**.—These result from the action of alcohols and haloid acids upon the aldehydes. Alcohols or alcoholates readily convert them into acetals. *Monochlormethyl Ether*, $CH_2<\begin{smallmatrix}O\,.\,C_2H_5\\Cl\end{smallmatrix}$, boils at 60°; D. $\frac{15}{4} = 1.1508$. *Monobrommethyl Ether* boils at 87°; sp. gr., 1.531 (12.5°). *Mono-iodomethyl Ether* boils at 124°; sp. gr., 2.0249 (15.9°) (B. **26**, R. 933). *Monochlormethyl-ethyl Ether*, $CH_2<\begin{smallmatrix}OC_2H_5\\Cl\end{smallmatrix}$, boils at 80°; D. $\frac{15}{4} = 1.023$. Consult B. **27**, R. 670, for higher monochlormethyl alkyl ethers.

a-Monochlorethyl Ether, $CH_3\,.\,CHCl\,.\,O\,.\,CH_2\,.\,CH_3$, boiling at 98°, and isomeric with ethylene chlorhydrinethyl ether, $ClCH_2\,.\,CH_2\,.\,O\,.\,C_2H_5$, is produced by the chlorination of ether, and by saturating a mixture of aldehyde and alcohol with hydrochloric acid, into which substances it is again resolved by water. *Monobromethyl Ether* boils at 105° (B. **18**, R. 322).

3. **Sym. *a*-Dihalogen Alkyl Ethers, Ethers of the Aldehyde Halohydrins.**—The symmetrical dihalogen methyl ethers result from the action of the haloid acids upon trioxymethylene. s-*Dichlormethyl Ether* $(CH_2Cl)_2O$, boils at 105°, and has the sp. gr. 1.315. s-*Dibrommethyl Ether* boils at 150°. s-*Di-iodomethyl Ether* boils at 218°.

C. **Carboxylic Esters of Methylene and Ethidene Glycols** are formed (1) from aldehydes and acid anhydrides; (2) from aldehydes and acid chlorides; (3) from the corresponding chlorides, bromides and iodides by the action of silver salts. When boiled with water these esters break down into aldehydes and acids:

$$
\begin{aligned}
&1.\quad CH_3\,.\,CHO + (CH_3CO)_2O = CH_3CH(OCOCH_3)_2\\
&2.\quad CH_3CHO + CH_3\,.\,COCl = CH_3CH<\begin{smallmatrix}O\,.\,COCH_3\\Cl\end{smallmatrix}\\
&3.\quad CH_2I_2 + 2CH_3\,.\,CO_2Ag = CH_2(OCOCH_3)_2 + 2AgI.
\end{aligned}
$$

Methylene Diacetic Ester, $CH_2(OCOCH_3)_2$, boils at 170°. **Ethidene Diacetate**, $CH_3CH(O\,.\,COCH_3)_2$, boils at 169°. **Ethidene Chlorhydrin Acetate,** *acetic monochlorethyl ester*, $CH_3\,.\,CH<\begin{smallmatrix}O\,.\,COCH_3\\Cl\end{smallmatrix}$, boiling at 121.5°, serves as starting-out material in the preparation of *ether esters* and *mixed esters*. **Ethidene Chlorhydrin Propionate**, $CH_3CH<\begin{smallmatrix}O\,.\,CO\,.\,C_2H_5\\Cl\end{smallmatrix}$, boils at 134–136°. By treating the first chlorhydrin with silver propionate there results the same **Ethidene Acetpropionate**, $CH_3\,.\,CH\,.<\begin{smallmatrix}O\,.\,CO\,.\,CH_3\\O\,.\,CO\,.\,CH_3\end{smallmatrix}$, boiling at 178.6°, as is obtained from the second by the action of *silver acetate*. *These facts argue for the equivalence of the carbon valences* (Geuther, A. **225**, 267).

3. SULPHUR DERIVATIVES OF THE LIMIT ALDEHYDES.

In this class are (A) the *thioaldehydes*, their *polymeric modifications* and their *sulphones;* (B) the *mercaptals* or *thioacetals*, with their *sulphones*, and (C) the *oxysulphonic* and *disulphonic acids* of the aldehydes.

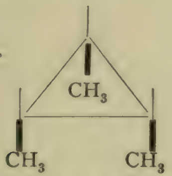
A. **Thioaldehydes, Polymeric Thioaldehydes and their Sulphones.**—The simple thioaldehydes are not well known. The polymeric thioaldehydes are more accessible. All of them can be regarded as the alkyl derivatives of polymeric trithioformaldehyde, the trithiomethylene, discovered by A. W. Hofmann. They are formed when the aldehydes are acted upon with H_2S and HCl. The H_2S adds itself to the $C=O$-group of the aldehydes, and *oxysulphhydrides* result, from which the trithioaldehydes arise:

$$CH_2O \xrightarrow{H_2S} CH_2<\begin{smallmatrix}SH\\OH\end{smallmatrix} \longrightarrow CH_2<\begin{smallmatrix}S\,.\,CH_2SH\\S\,.\,CH_2OH\end{smallmatrix} \longrightarrow CH_2<\begin{smallmatrix}S-CH_2\\S-CH_2\end{smallmatrix}>S.$$

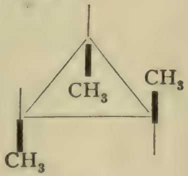
The trithioaldehydes are odorless solids, whereas the simple thioaldehydes and their mercaptan-like transposition products possess an adherent, disagreeable odor. Potassium permanganate oxidizes the trithioaldehydes first to *sulphide-sulphones* and then to *trisulphones*. The molecular weight of the trithioaldehydes has been determined both by vapor density and by the lowering of the freezing point of their naphthalene solution. Klinger first proposed the structure for the trithioaldehydes. It corresponds to the formula of paraldehyde and was proved correct by the oxidation of the trithioaldehydes to trisulphones.

The isomeric phenomena of the trithioaldehydes led Baumann and Fromm to consider their spacial relations (B. **24**, 1426).

Proceeding from the same considerations, which served Baeyer in his explanation of the isomerism of the hexamethylene derivatives (see *hexahydrophthalic acids*), these chemists distinguished *a*-, *cis*- or maleïnoid and *β*-, *trans*- or fumaroïd modifications. Camps endeavors to represent the spacial difference between two trithioaldehydes in the following way:



a, Cis-form.



β, Trans-form.

The C-atoms are assumed to be in the angles of the triangles, and the S-atoms are in the middle of the sides. The three alkyl groups are either upon the same side of the six-membered ring system: *a*, *cis*-form; or upon different sides of it: *β*, *trans*-modification. Only one disulphone-sulphide corresponds to the *cis*-modification, while *two* stereo-isomeric disulphone-sulphides take the *trans*-form (see Klinger, B. **11**, 1027).

Trithioformaldehyde, $[CH_2S]_3$, melts at 216°. **Thioacetaldehyde** is not known in a pure state. *a*-**Trithioacetaldehyde** melts at 101° and boils at 246–247°. Acetyl chloride converts it into *β*-**trithioacetaldehyde**, $[CH_3CHS]_3$, melting at 125–126°, and boiling at 245–248° (B. **24**, 1457).

Sulphones of the Trithioaldehydes.—The trisulphones, resulting from the oxidation of the trithioaldehydes, are all to be viewed as alkylized derivatives of *trimethylene trisulphone*. The six methylene hydrogen atoms of trimethylene trisulphone are acid like those of the methylenes in *malonic ester* (see this). They can be replaced by metals, and hexa-alkylized trimethylene sulphones can be synthetically prepared by the double decomposition of the alkali derivatives with alkyl iodides. These are identical with the oxidation products of the corresponding *trithioketones*. The primary product in the oxidation of a trithioaldehyde is a monosulphone, the secondary a disulphone, and finally a trisulphone is produced.

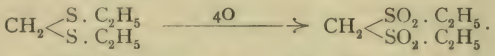
Trimethylene Trisulphone, $CH_2{<}\begin{smallmatrix}SO_2—CH_2\\SO_2—CH_2\end{smallmatrix}{>}SO_2$, and **Trimethylene Disulphone-sulphide**, $CH_2{<}\begin{smallmatrix}SO_2\,.\,CH_2\\SO_2\,.\,CH_2\end{smallmatrix}{>}S$, do not melt at 340°. This is also true of **Triethidene Trisulphone**, $[CH_3CHSO_2]_3$ (B. **25**, 248).

The two isomeric trithioacetaldehydes yield **Triethidene Disulphone-sulphide**, $CH_3\,.\,CH\,.{<}\begin{smallmatrix}SO_2CH(CH_3)\\SO_2CH(CH_3)\end{smallmatrix}{>}S$, melting at 228–231°. "The isomerism of the trithioaldehydes vanishes in their oxidation products" (B. **26**, 2074; **27**, 1667).

Thialdin, $CH_3\ CH{<}\begin{smallmatrix}S\,.\,CH(CH_3)\\S\,.\,CH(CH_3)\end{smallmatrix}{>}NH$, melting at 43°, is produced by the action of NH_3 upon *a*-trithioacetaldehyde (B. **19**, 1830), and of H_2S upon aldehyde-ammonia (A. 61, 2). It yields *ethidene disulphonic acid* (see below) by oxidation. **Methyl Thialdin**, $(C_2H_4)_3S_2(NCH_3)$, melts at 79° (B. 19, 2378).

B. Mercaptals or Thioacetals and their Sulphones.

The *thioacetals*, corresponding to the *acetals*, are called *mercaptals*. They are formed (1) from alkyl iodides and alkali mercaptides; (2) by the action of HCl upon the aldehydes and mercaptans. They are oils with very unpleasant odors, and are oxidized by $KMnO_4$ to sulphones:



$$CH_2{<}\begin{matrix}S\,.\,C_2H_5\\S\,.\,C_2H_5\end{matrix}\xrightarrow{4O}CH_2{<}\begin{matrix}SO_2\,.\,C_2H_5\\SO_2\,.\,C_2H_5\end{matrix}.$$

Methylene Mercaptal, $CH_2(SC_2H_5)_2$, boils at about 180°. **Ethidene Mercaptal**, ethidene dithioethyl, *dithioacetal*, $CH_3\,.\,CH\,.\,(SC_2H_5)_2$, boils at 186°. **Propidene Mercaptal**, $CH_3\,.\,CH_2\,.\,CH(SC_2H_5)_2$, boils at 198°.

In the sulphones of the mercaptals the methylene hydrogen (see above) is replaceable by alkali metal. Mono- and dialkylized sulphones can be prepared from these alkali derivatives. Again, the dialkylized sulphones may be obtained from the *mercaptols* (p. 218); *sulphonal* belongs to this class.

Methylene Diethyl Sulphone, $CH_2(SO_2C_2H_5)_2$, melting at 104°, is readily soluble in water and in alcohol. It is formed in the oxidation of orthothioformic ethyl ether (see this). *Ethidene Diethyl Sulphone*, $CH_3CH(SO_2C_2H_5)_2$, melts at 75° and boils without decomposition at about 320°.

C. Oxysulphonic Acids and Disulphonic Acids of the Aldehydes.

The alkali salts of the oxysulphonic acids crystallize well. They decompose quite easily and are formed by the action of the alkali bisulphites upon the aldehydes. Acids decompose them into aldehydes and SO_2.

The only stable acid is—

Methylenehydrin Sulphonic Acid, Oxymethylene Sulphonic Acid, $CH_2(OH)SO_3H$, which is formed together with **Oxymethylene Disulphonic Acid**, $CH(OH)(SO_3H)_2$, and **Methine Trisulphonic Acid**, $CH(SO_3H)_3$, by the action of fuming sulphuric acid upon methyl alcohol and subsequent boiling of the product with water.

Methionic Acid, of the disulphonic acids of the aldehydes, has long been known: **Methylene Disulphonic Acid**, $CH_2\,.\,(SO_3H)_2$, **Methionic Acid**, is produced when fuming sulphuric acid acts upon *acetamide*, *acetonitrile*, *lactic acid*, etc. It is most conveniently made by saturating fuming sulphuric acid with acetylene (from calcium carbide). In this instance it is most certainly due to the decomposition of *acetaldehyde-disulphonic acid*, an intermediate product:

$$CH\,\vdots\,CH\xrightarrow[H_2O]{2SO_3}OCH\,.\,CH(SO_3H)_2\xrightarrow{\qquad}CH_2(SO_3H)_2+CO.$$

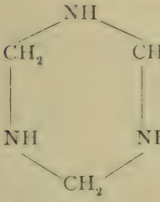
There is simultaneously formed another sulpho-acid, richer in carbon. It can easily be separated from this by means of its sparingly soluble barium salt. (Privately communicated by G. Schroeter.) Methionic acid crystallizes in deliquescent needles. It is not decomposed by boiling nitric acid. $CH_2(SO_3)_2Ba + 2H_2$ Oconsists of pearly leaflets, dissolving with difficulty in water. **Ethidene Disulphonic Acid**, $CH_3\,.\,CH(SO_3H)_2$, is produced when *thialdin* is oxidized with $KMnO_4$ (B. 12, 682). The hydrogen of the methine group in **Ethidene Disulphonic Acid Ethyl Ester**, $CH_3\,.\,CH(SO_3C_2H_5)_2$, can be replaced by sodium by means of sodium alcoholate, and then by alkyls, just as was done in the case of the sulphones (p. 203) and the alkyl malonic esters (see these) (B. 21, 1550).

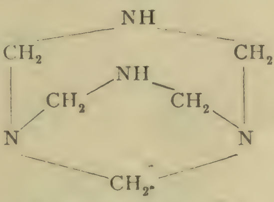
4. NITROGEN DERIVATIVES OF THE ALDEHYDES.

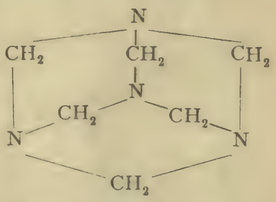
A. **Nitro-Compounds.**—*Brom-nitromethane*, and 1,1-*brom-nitroethane* and *propane*, as well as 1,1-dinitro-paraffins, which have been previously described, must be regarded as nitrogen-containing aldehyde derivatives.

B. **Ammonia- and Monalkylamine Aldehyde Derivatives** (p. 192).—While ammonia adds itself to acetaldehyde and its homologues, forming aldehyde ammonias or amido-alcohols, *e. g.*, $CH_3 . CH{<}^{NH_2}_{OH}$, when it comes in contact with formaldehyde it immediately produces—

Hexamethylenetetramine, $(CH_2)_6N_4$, discovered in 1860 by Butlerow. Under the name of *formin* it is used as a solvent for uric acid. It is very soluble in water. It crystallizes from alcohol in brilliant rhombohedra. It sublimes without decomposition in a vacuum. It is again resolved into CH_2O and ammonia when distilled with sulphuric acid. It is a monacid base, but shows no reaction with litmus (B. **22**, 1929). It combines with the alkyl iodides (B. **19**, 1840). (Consult further B. **26**, R. 238.) Efforts have been made to ascertain its molecular weight by the analysis of its salts, by an approximate determination of its vapor density, and by the lowering of the freezing point of its aqueous solution (B. **19**, 1842; **21**, 1570). Nitrous acid first converts hexamethylenetetramine into dinitrosopentamethylenetetramine, and this then into trinitrosotrimethylenetriamine. When it is considered that trimethylenetrimethyltriamine is formed by the interaction of methylamine and formaldehyde, it is obvious that the reaction must cease at this point, because the imide-hydrogen atoms have been replaced by methyl groups. Ammonia and formaldehyde yield at first trimethylenetriamine, corresponding to trimethylenetrimethyltriamine, which absorbs ammonia and formaldehyde, splits off water and becomes pentamethylenediamine. The latter is converted by formaldehyde into hexamethylenetetramine The following constitutional formulas aim to represent this deportment (compare Roscoe-Schorlemmer (1884), vol. III, 646; Duden and Scharff, A. **288**, 218):


Trimethylenetriamine


Pentamethylenetetramine


Hexamethylenetetramine.

The following bodies are produced when primary amines act upon formaldehyde (B. **28**, R. 233, 381, 924; **29**, 2110):

Methylmethyleneamine, $[CH_2 = N . CH_3]_3$, boiling point, 166°; sp. gr., 0.9215 (18.7°).

Ethylmethyleneamine, $[CH_2 = N . C_2H_5]_3$, boiling point, 207°; sp. gr., 0.8923 (18.7°).

n-**Propylmethyleneamine**, $[CH_2 = N . C_3H_7]_3$, boiling point, 248°; sp. gr., 0.880 (18.7°).

By the use of aldehydes with higher molecular weight, the tendency to polymerization on the part of the reaction products of primary amines and aldehydes diminishes:

Methylisobutyleneamine, $(CH_3)_2CH . CH = N . CH_3$, boils at 68°. Secondary amines and formaldehyde yield—

Tetramethylmethylenediamine, $CH_2{<}^{N(CH_3)_2}_{N(CH_3)_2}$, boiling at 85° (B. **26**, R. 934).

Aldehyde-ammonia, $CH_3CH(OH)NH_2$, melts at 70–80° and boils at 100°. It is produced when dry ammonia gas is conducted into an ethereal solution of aldehyde, and consists of brilliant rhombohedra, dissolving readily in water. They can be vaporized without decomposition in a vacuum. Acids resolve it into its components (p. 192):

$$CH_3 . CHO \xrightarrow{NH_3} CH_3 . CH(OH)NH_2 \xrightarrow{SO_4H_2} CH_3CHO + SO_4H . NH_4.$$

In contact with water it passes into amorphous *Hydracetamide*, $C_6H_{12}N_2$. Sodium nitrite, added to a slightly acidulated solution of aldehyde-ammonia, produces—

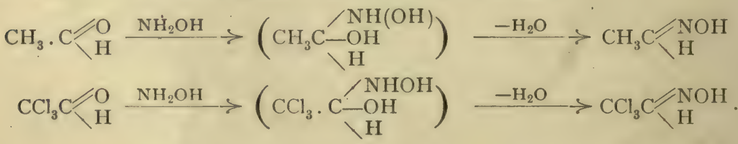
Nitrosoparaldimine, $C_6H_{12}O_2(N.NO)$, which by reduction becomes amidoparaldimine, $C_6H_{12}O_2(N.NH_2)$, and this in turn, by the action of dilute sulphuric acid, splits off *Hydrazine*, $NH_2.NH_2$ (B. **23**, 740). Paraldimine should be viewed as paraldehyde in which an oxygen atom has been replaced by the imido group. Hydrogen sulphide changes aldehyde-ammonia to *Thialdin* (p. 203), while with prussic acid it becomes the nitrile of *a-amidopropionic acid* (see this). A rather remarkable reaction occurs when aldehyde-ammonia acts upon aceto-acetic ester. It is the formation of 1, 3, 5-*Trimethyldihydropyridine-dicarbonic ester* (see this).

Chloral-ammonia, $CCl_3CH<\begin{smallmatrix}NH_2\\OH\end{smallmatrix}$, melts at 63°.

For the *chloralimides*, $(CCl_3.CH:NH)_3$, and *Dehydrochloralimides*, $C_6H_4Cl_9N_3$, consult B. **25**, R. 794; **24**, R. 628. The isomerism of the former is very probably dependent upon the same causes as that of the polymeric thioaldehydes (p. 203).

C. Aldoximes, $R'.CH=N.OH$ (V. Meyer, 1863).

The aldoximes are formed when hydroxylamine, an aqueous solution of the hydrochloride (1 mol.), mixed with an equivalent quantity of soda (½ mol.) acts in the cold upon aldehydes. At first there is very evidently formed an unstable addition product, corresponding to aldehyde-ammonia, which in the case of chloral may be obtained in stable form, but which passes readily into the oxime:



$$CH_3.C\begin{smallmatrix}\nearrow O\\ \searrow H\end{smallmatrix} \xrightarrow{NH_2OH} \left(CH_3C\begin{matrix}/NH(OH)\\ -OH\\ \backslash H\end{matrix}\right) \xrightarrow{-H_2O} CH_3C\begin{smallmatrix}\nearrow NOH\\ \searrow H\end{smallmatrix}$$

$$CCl_3C\begin{smallmatrix}\nearrow O\\ \searrow H\end{smallmatrix} \xrightarrow{NH_2OH} \left(CCl_3.C\begin{matrix}/NHOH\\ -OH\\ \backslash H\end{matrix}\right) \xrightarrow{-H_2O} CCl_3C\begin{smallmatrix}\nearrow NOH\\ \searrow H\end{smallmatrix}.$$

The aldoximes are colorless liquids which boil without decomposition. The first members of the series dissolve readily in water. When boiled with acids they are again changed to aldehyde and hydroxylamine. By the action of acetic anhydride or acetyl chloride the aldoximes become nitriles:

$$\underset{\text{Acetoxime}}{CH_3CH=NOH} + (CH_3CO)_2O = \underset{\text{Acetonitrile.}}{CH_3CN} + 2CH_3CO_2H.$$

The oximes and hydrazones (p. 207), like the aldehydes, take up prussic acid; the products are amidoxyl- or hydrazino-nitriles (B. **29**, 62)

Formoxime, *Formaldoxime*, $CH_2=N.OH$, boils at 84°, and passes spontaneously into polymeric triformoxime, $CH_2<\begin{smallmatrix}N(OH).CH_2\\N(OH).CH_2\end{smallmatrix}>N.OH$ (B. **29**, R. 658). Formoxime yields hydrocyanic acid when it is boiled with water (B. **28**, R. 233).

Acetaldoxime, $CH_3.CH:NOH$, melting at 47° and boiling at 115°, also exists in a second modification, melting at 12°, which readily reverts to the first form (B. **26**, R. 610; **27**, 416).

Chloralhydroxylamine, $CCl_3.CH(OH)NH(OH)$, melts at 89° (B. **25**, 702), and even upon standing in the air becomes—

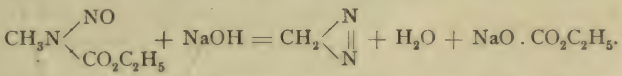
Chloraloxime, $CCl_3CH=NOH$, melting at 39–40°.

Propionaldoxime, $C_2H_5.CH=N.OH$, boils at 130–132°.

Isobutyraldoxime, $(CH_3)_2CH.CH=NOH$, boils at 139°. **Isovaleraldoxime**, $(CH_3)_2CH.CH_2.CH=NOH$, boils at 164–165°. **Œnanthaldoxime**, $CH_3(CH_2)_5$-$CH:NOH$, melts at 55.5° and boils at 195°. **Myristinaldoxime** melts at 82° (B. **26**, 2858). The aldoximes of the fat series resemble the aromatic synaldoximes in their deportment (B. **28**, 2019).

D. **Diazoparaffins** are produced, as shown by v. Pechmann in 1894, by the action of alkalies upon nitrosamines. Diazomethane alone has been carefully studied.

Diazomethane, *Azimethylene*, CH_2N_2, is at the ordinary temperature a yellow, odorless, but very poisonous gas, which strongly attacks the skin, the eyes, and the lungs. It is best made by the action of alkalies upon nitrosomethylurethane:



$$CH_3N\left\langle\begin{matrix}NO\\CO_2C_2H_5\end{matrix}\right. + NaOH = CH_2\left\langle\begin{matrix}N\\\|\\N\end{matrix}\right. + H_2O + NaO \, . \, CO_2C_2H_5.$$

Diazomethane exhibits the reactivity of diazoacetic ester (see this). Water converts it into methyl alcohol. Iodine changes it to methylene iodide. Inorganic and organic acids are changed into their methyl esters: hydrochloric acid into methyl chloride; prussic acid into acetonitrile; phenols into anisols; toluidine into methyl toluidine. Diazomethane and fumaric methyl ester unite to pyrazolindicarboxylic ester (B. **28**, 1624, 2377).

E. Aldehyde Hydrazones (E. Fischer, A. **190**, 134; **236**, 137).

The *aldehyde hydrazones* correspond to the *aldoximes*. They are the transposition products of aldehydes and *hydrazines* (see these), which are formed when their constituents are mixed in ethereal solution. The water produced in the reaction is removed by K_2CO_3, and the hydrazones then purified by distillation under diminished pressure:

$$CH_3CHO + H_2N \, . \, NHC_6H_5 = CH_3CH = N \, . \, NHC_6H_5 + H_2O.$$

Acetaldehyde Hydrazone, Ethidene Phenylhydrazine, $CH_3 \, . \, CH = NNHC_6H_5$, boils at 140° (20 mm.). Crystals, melting at 63–65°, separate from the cold solution of the freshly distilled preparation, dissolved in 75 per cent. alcohol. If the liquid, after the addition of 4 c.c. of conc. sodium hydroxide, be heated to boiling for three minutes, a second modification, melting at 98–101°, will separate out upon cooling. When azophenylethyl (see this) is dissolved in cold, concentrated sulphuric acid, it changes to acetaldehydephenylhydrazone (B. **29**, 793). Aldehyde precipitates the body $CH_3 \, . \, CHO \, . \, 2(C_6H_5NHNH_2)$, melting at 77.5°, from the solution of phenylhydrazine bitartrate (B. **29**, R. 596). *Propylaldehydephenylhydrazone*, $CH_3 \, . \, CH_2 \, . \, CH = N_2C_6H_5$, boils at 205° (180 mm.). These hydrazones take up prussic acid and pass into the nitriles of hydrazido-acids (B. **25**, 2020).

Formaldehyde differs from the higher homologues in that with phenylhydrazine it yields—

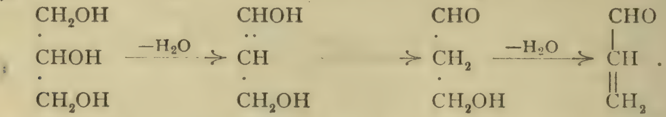
Trimethylene Phenylhydrazine, $(C_6H_5N_2)_2(CH_2)_3$, melting at 183–184° (B. **29**, 1473; R. 777).

Formalazine, $CH_2 = N — N = CH_2$ (?), from formaldehyde and hydrazine, is a white, amorphous, somewhat hygroscopic mass (B. **26**, 2360).

2 B. OLEFINE ALDEHYDES, $C_nH_{2n-1} \, . \, CHO$.

The unsaturated aldehydes, having a double carbon union, bear the same relation to the olefine alcohols (p. 130) that the paraffin aldehydes sustain to their corresponding alcohols. Their aldehyde group shows the same reactive power as the group in the ordinary aldehydes. In addition, the unsaturated residue, C_nH_{2n-1}, gives rise to addition-reactions similar to those shown by the olefines. Some of the olefine aldehydes are connected with the saturated aldehydes by condensation reactions; *e. g.*, crotonaldehyde, tiglic aldehyde, methyl acroleïn, etc.

Acroleïn, $C_3H_4O = CH_2 : CH . CHO$, boils at 52°. It is produced by the oxidation of allyl alcohol and by the distillation of glycerol or fats (1 pt.) with potassium bisulphate (2 pts.) (B. **20**, 3388; A. Sup. **3**, 180):



$$\begin{array}{ccccccc} CH_2OH & & CHOH & & CHO & & CHO \\ \cdot & & \cdot\cdot & & \cdot & & | \\ CHOH & \xrightarrow{-H_2O} & CH & \rightarrow & CH_2 & \xrightarrow{-H_2O} & CH \\ \cdot & & \cdot & & \cdot & & \| \\ CH_2OH & & CH_2OH & & CH_2OH & & CH_2 \end{array} .$$

Acroleïn is a colorless, mobile liquid, possessing a sp. gr. of 0.8410 at 20°. It has a pungent odor and attacks the mucous membranes in a frightful manner. It is soluble in 2–3 parts water. It reduces an ammoniacal silver solution, with formation of a mirror-like deposit, and when exposed to the air it oxidizes to acrylic acid. It does not combine with primary alkaline sulphites. Nascent hydrogen converts it into *allyl alcohol* (p. 130).

Phosphorus pentachloride converts acroleïn into propylene dichloride, $CH_2 : CH . CHCl_2$, boiling at 84° C. With hydrochloric acid it yields β-chlorpropionic aldehyde (p. 199). With bromine it yields a dibromide, $CH_2 . Br . CHBr . CHO$, which becomes α,β-dibrompropionic acid upon oxidation with nitric acid. Baryta water converts it into *a-acrose* or (d + l)-fructose (see this).

When preserved, acroleïn passes into an amorphous, white mass (*disacryl*). On warming the HCl compound of acroleïn (see above) with alkalies or potassium carbonate *metacroleïn* is obtained. The vapor density of this agrees with the formula $(C_3H_4O)_3$. It fuses at 45–46°.

Ammonia changes acroleïn to the so-called *acroleïn-ammonia*, $2C_3H_4O + NH_3 = C_6H_9NO + H_2O$. This is a yellowish mass that on drying becomes brown, and forms amorphous salts with acids. It yields *picoline*, C_6H_7N (methylpyridine, $C_5H_4 . N . CH_3$), when distilled. Hydrazine changes acroleïn to pyrazoline, and phenylhydrazine converts it into 1-phenylpyrazoline (B. **28**, R. 69).

Crotonaldehyde, $C_4H_6O = CH_3 . CH : CH . CHO$, boils at 104° (Kekulé, A. **162**, 91). It is obtained by the condensation of *acetaldehyde* (p. 195) from the primarily formed *aldol* when heated with dilute hydrochloric acid, with water and zinc chloride, or with a sodium acetate solution, to 100° C. (B. **14**, 514; **25**, R. 732). When aldol is heated or treated with dilute hydrochloric acid it splits off water and becomes crotonaldehyde:

$$2CH_3.CHO \longrightarrow CH_3.CH(OH).CH_2.CHO \longrightarrow CH_3.CH = CH.CHO.$$

Crotonaldehyde is a liquid with irritating odor; at 0° it has a sp. gr. of 1.033 and boils at 104°. On exposure to the air it oxidizes to crotonic acid; it reduces silver oxide (B. **29**, R. 290). It combines with hydrochloric acid to form *β-chlorbutyraldehyde* (p. 199); on standing with hydrochloric acid it unites with water and becomes *aldol*. Iron and acetic acid change it to *croton-alcohol*, *butyraldehyde* and *butyl alcohol*.

When the alcoholic solution of acetaldehyde-ammonia is heated to 120°, **Crotonal-ammonia,** $C_8H_{13}NO$ (**Oxtetraldine**), is produced. It is a brown, amorphous mass. When heated it breaks up into water and **collidine,** $C_8H_{11}N$ (see this).

Tiglic Aldehyde, guaiacol, $CH_3CH = C(CH_3) . CHO$, boils at 116°. It may be obtained by the distillation of guaiacol resin and by the condensation of ethyl- and propyl-aldehydes.

Methyl-ethyl Acroleïn, $C_2H_5 . CH : C(CH_3) . CHO$, is produced by the condensation of propionic aldehyde (p. 196), and boils at 137° C.

Citronellal and its isomeride **Rhodinal** are olefine aldehydes, and **Geranial** or **Citral** belongs to the class of diolefine aldehydes. These will be duly considered under the *olefine terpenes*.

2 C. **Acetylene Aldehydes,** $C_nH_{2n-3} . CHO$. **Propargylic Aldehyde,** $CH \vdots C . CHO$, boils at 59°. It is produced when the *acetal*, $CH \vdots C . CH(OC_2H_5)_2$, boiling at 140°, from dibrom-acroleïn acetal and alcoholic potash, is boiled with dilute sulphuric acid. It is a very mobile liquid, which provokes tears. Its *silver salt* is very explosive. Sodium hydrate at the ordinary temperature decomposes propargylic aldehyde instantly into acetylene and sodium formate: $CH \vdots C . CHO + NaOH = CH \vdots CH + NaO . CHO$ (L. Claisen, privately communicated).

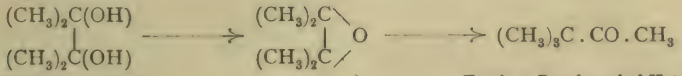
3 A. Ketones of the Limit Series, Paraffin Ketones, $C_nH_{2n}O$.

In the introduction to the aldehydes and ketones (p. 187) attention was directed to the great similarity between these two classes of compounds, which finds expression in their most important methods of formation and in their transposition reactions. It was also there stated that two different kinds of ketones were known:

1. *Simple ketones*, containing two similar alkyls.
2. *Mixed ketones*, having two different alkyls.

Methods of Formation.—1. Oxidation of secondary alcohols, whereby the $= CH . OH$-group is transposed to the $= CO$-group (p. 187).

2. A variety of ketones, the *pinacolines*, is obtained from the ditertiary glycols—the *pinacones* (see these)—by the withdrawal of water. This is effected by means of hot hydrochloric acid or hot dilute sulphuric acid. The simplest ditertiary glycol is *tetramethyl glycol*, or *pinacone*. It might be expected that when this lost water, *tetramethyl-ethylene oxide* would be produced. However, by the occurrence of a remarkable intramolecular atomic rearrangement it yields the simplest *pinacoline*, *tertiary butyl-methyl ketone:*



$$\begin{array}{c}(CH_3)_2C(OH)\\ |\\ (CH_3)_2C(OH)\end{array} \longrightarrow \begin{array}{c}(CH_3)_2C\diagdown\\ |\quad O\\ (CH_3)_2C\diagup\end{array} \longrightarrow (CH_3)_3C . CO . CH_3$$

Tetramethyl Glycol
Pinacone

Tertiary Butyl-methyl Ketone,
Pinacoline.

3. By heating the ketone chlorides with water:

$$(CH_3)CCl_2 \xrightarrow[100^\circ]{H_2O} (CH_3)_2CO.$$

4. By action of acids (B. 29, 202) upon the sodium salts of the mononitroparaffins (pp. 156, 157), in which the nitro-group is attached to a terminal carbon atom:

$$2(CH_3)_2C{<}^{NO_2}_{Na} + 2HCl = 2(CH_3)_2CO + N_2O + 2NaCl + H_2O.$$

Nucleus-synthetic Methods of Formation.—5. By the distillation of calcium or barium acetates and their higher homologues. Such a salt, when heated alone, yields a *simple ketone*. The distillation of a mixture of equimolecular quantities of the salts of two acids results in the formation of *mixed ketones* (p. 188).

In making ketones with high molecular weight it is best to carry out the distillation under diminished pressure. Some normal fatty acids have yielded ketones on treatment with P_2O_5 (B. **26**, R. 495).

6. The action of the zinc alkyls upon the chlorides of the acid radicals (Freund, 1860).

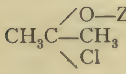
The reaction is similar to that occurring in the formation of the tertiary alcohols (p. 114). At first the same intermediate product is produced (A. 175, 361; 188, 104):

$$CH_3.COCl + Zn(CH_3)_2 = CH_3.C\left\{\begin{array}{l}CH_3\\ O.Zn.CH_3,\\ Cl\end{array}\right.$$

which (with a second molecule of the acid chloride) afterwards yields the ketone and zinc chloride:

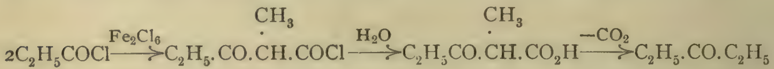
$$CH_3.C\left\{\begin{array}{l}CH_3\\ O.Zn.CH_3\\ Cl\end{array}\right. + CH_3.COCl = 2CH_3.CO.CH_3 + ZnCl_2.$$

In many cases, especially in the preparation of pinacolines from trimethyl-acetyl chloride and zinc methide, it is more advantageous to immediately decompose the addition product of zinc methide and acid chloride with water, when the zinc hydroxide will be transposed by the hydrochloric acid into zinc chloride:



$$CH_3C\begin{array}{l}\diagup O-ZnCH_3\\ -CH_3\\ \diagdown Cl\end{array} + 2H_2O = CH_3.CO.CH_3 + Zn(OH)_2 + HCl + CH_4.$$

7. By the action of anhydrous ferric chloride upon the acid radicals. Hydrochloric acid is evolved, and chlorides of β-ketone carboxylic acids are produced. From these water liberates the free β-ketone carboxylic acids. The latter break down readily into carbonic acid and ketones (compare method of formation 8):

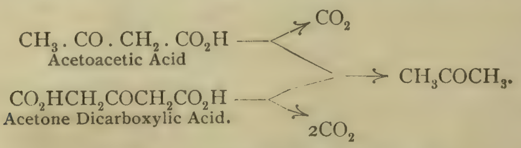


$$2C_2H_5COCl \xrightarrow{Fe_2Cl_6} C_2H_5.CO.\overset{\overset{\displaystyle CH_3}{\cdot}}{C}H.COCl \xrightarrow{H_2O} C_2H_5CO.\overset{\overset{\displaystyle CH_3}{\cdot}}{C}H.CO_2H \xrightarrow{-CO_2} C_2H_5.CO.C_2H_5$$

8. By the oxidation of dialkyl acetic acids, and the α-oxydialkyl-acetic acids corresponding to them; the latter are simultaneously formed as intermediate products in the oxidation of the former compounds, *e.g.*:

$$(CH_3)_2CH.CO_2H \xrightarrow{O} (CH_3)_2C(OH).CO_2H \xrightarrow{O} (CH_3)_2CO + CO_2 + H_2O.$$

9. By the breaking down of β-ketone mono- and dicarboxylic acids—*e. g.*:



Compare acetoacetic ester, and also acetone dicarboxylic acid.

The ketones are produced in the dry distillation of citric acid, sugar, cellulose (wood), and many other carbon compounds.

Nomenclature and Isomerism.—The term ketone is derived from the simplest and first discovered ketone—*acetone*. The names of the ketones are obtained by combining the names of the alkyls with the syllable *ketone*—*e. g.*, dimethyl ketone, methyl-ethyl ketone, etc.

A. Baeyer regards the ketones as keto-substitution products of the hydrocarbons, and the group CO, uniting two alkyl groups, he terms the keto-group. As one carbon atom in the name ketopropane would, in consequence of this suggestion, be twice designated, Kekulé has suggested that the oxygen linked doubly to carbon be called "oxo"-oxygen. Then acetone, CH_3COCH_3, would be 2-*oxopropane*, propionic aldehyde, $CH_3 . CH_2 . CHO$, would be 1-*oxopropane*. The "Geneva names" are obtained by adding the suffix "on" to the name of the hydrocarbon: acetone is called [Propanon], and methyl-ethyl ketone is [Butanon].

As there is a ketone for every secondary alcohol, the number of isomeric ketones of definite carbon content is equal to the number of possible secondary alcohols containing the same number of carbon atoms. The *simple ketones* are isomeric with the *mixed ketones* having a like carbon content. The isomerism of the ketones among themselves is dependent upon the homology of the alcohol radicals united with the CO-group. Consult the isomerism of the aldehydes (p. 190) for the isomerism of the ketones with other compounds.

Properties and Transformations.—The ketones are neutral bodies. The lower members of the series are volatile, ethereal-smelling liquids, while the higher members are solids.

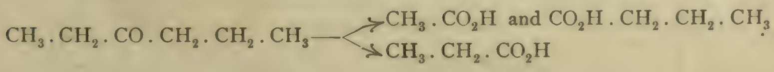
In enumerating the transpositions possible with ketones, it will be best to present *acetone*, the most important and most thoroughly investigated member of this class of bodies.

1. Ketones differ chiefly from aldehydes in their behavior when oxidized. They are not capable of reducing an alkaline silver solution. They are not so easily oxidized as the aldehydes.

When more powerful oxidants are employed, the ketones almost invariably break down at the union with the CO-group. Carboxylic acids are produced, and in some cases ketones with a lower carbon content:

$$CH_3 . CO . CH_3 \longrightarrow CH_3 . CO_2H \text{ and } H . CO_2H \xrightarrow{O} CO_2 + H_2O.$$
$$C_2H_5 . CO . C_2H_5 \longrightarrow C_2H_5 . CO_2H \text{ and } CH_3 . CO_2H.$$

In the case of mixed ketones, when both alcohol radicals are primary in character, the CO-group does not, as was formerly supposed, remain exclusively with the lower alcohol radical, but the reaction proceeds in both possible directions, *e. g.*:



$$CH_3 . CH_2 . CO . CH_2 . CH_2 . CH_3 \begin{array}{l} \nearrow CH_3 . CO_2H \text{ and } CO_2H . CH_2 . CH_2 . CH_3 \\ \searrow CH_3 . CH_2 . CO_2H \end{array}$$

When a secondary alcohol radical is present it splits off as ketone, and is then further oxidized, whereas in the case of a tertiary alcohol radical the CO-group remains combined as carboxyl.

The direction in which the oxidation proceeds is dependent less upon the oxidizing agent than upon the oxidation temperature (A. 161, 285; 186, 257; B. 15, 1194; 17, R. 315; 18, 2266, R. 178; 25, R. 121).

It is remarkable that *pinacoline* (p. 209) was successfully oxidized by potassium permanganate to the corresponding α-ketone carboxylic acid of like carbon content: *trimethyl pyroracemic acid*:

$$\underset{\text{Pinacoline}}{(CH_3)_3C\,.\,CO\,.\,CH_3} \xrightarrow{3O} \underset{\text{Trimethyl-pyroracemic Acid.}}{(CH_3)_3C\,.\,CO\,.\,CO_2H.}$$

2. Concentrated nitric acid breaks the ketones down, and converts them in part into dinitro-paraffins (p. 159):

$$(C_2H_5)_2CO \xrightarrow{NO_3H} CH_3CH(NO_2)_2$$
$$(CH_3\,.\,CH_2\,.\,CH_2)_2CO \longrightarrow CH_3\,.\,CH_2CH(NO_2)_2.$$

3. Amyl nitrite, in the presence of sodium ethylate or hydrochloric acid, converts the ketones into *isonitroso-ketones*:

$$CH_3\,.\,CO\,.\,CH_3 \xrightarrow{NOOC_5H_{11}} CH_3\,.\,CO\,.\,CH(NOH)$$
$$CH_3CO\,.\,CH_2\,.\,CH_3 \longrightarrow CH_3\,.\,CO\,.\,C(NOH)\,.\,CH_3.$$

The isonitroso-ketones will be discussed later as the *monoximes* of *α-keto-aldehydes* or *α-diketones*.

Many of the addition reactions possible with ketones are due, as in the case of the aldehydes, to the ready destruction of the double union between carbon and oxygen. These reactions are partly followed, even with the ketones, by an immediate exit of water.

4. Nascent hydrogen (sodium amalgam) converts the ketones into *secondary alcohols* (p. 113), from which they are produced by oxidation. *Pinacones*, or ditertiary glycols, are simultaneously formed (p. 209):

$$(CH_3)_2CO + 2H = (CH_3)_2CH\,.\,OH.$$

5. The ordinary ketones, like the ordinary aldehydes, are little disposed to combine with *water*. Acetones, containing numerous halogen atoms, unite with $4H_2O$ and $2H_2O$, forming hydrates.

The ketone derivatives, corresponding to the *acetals* (p. 200), are produced when the β-dialkyloxycarboxylic acids split off CO_2, and by the interaction of ketones and orthoformic ether (Claisen).

6. The ketones resemble the aldehydes in their deportment—

a. With hydrogen sulphide;

b. With mercaptans in the presence of hydrochloric acid.

The products are *polymeric thioketones* (p. 218), and the *mercaptols, e. g.*, $(CH_3)_2C(SC_2H_5)_2$, corresponding to the mercaptals (p. 204).

7. The ketones, unlike the aldehydes, do *not* combine with the acid anhydrides. Pinacoline alone unites with acetic anhydride to form a diacetate, melting at 65° (B. 26, R. 14).

8. Only those ketones, which contain a methyl group, form crys-

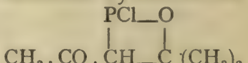
talline compounds with the alkaline bisulphites. These can be considered as salts of oxysulphonic acids:

$$(CH_3)_2CO + SO_3HNa = (CH_3)_2C{<}^{OH}_{SO_3Na}.$$

These double salts serve well for the isolation and purification of the ketones, which can be liberated from them by dilute sulphuric acid or a soda solution.

9. Behavior of ketones with ***ammonia***, ***hydroxylamine*** and ***phenylhydrazine***. (*a*) Acetone behaves differently toward ammonia from the aldehydes. Nucleus-synthetic reactions occur, with the formation of ***diacetonamine*** and ***triacetonamine*** (p. 219). With hydroxylamine, however, the ketones yield (*b*) ***ketoximes*** (p. 219) and (*c*) with phenylhydrazine they form ***hydrazones*** (p. 220). In these respects they resemble the aldehydes (p. 207).

10. When phosphorus trichloride acts upon acetone hydrochloric acid is evolved, and there results the compound



$$\begin{array}{l}\qquad\qquad\quad PCl{-}O \\ \qquad\qquad\quad\ \,|\qquad| \\ CH_3.CO.CH{-}C(CH_3)_2\end{array}$$

(B. **17**, 1273; **18**, 898).

11. *Phosphorus pentachloride*, *phosphorus trichlor-dibromide*, and *phosphorus tribromide* replace the oxygen of the ketones by two chlorine or two bromine atoms.

This reaction answers for the preparation of dichlor- or dibrom-paraffins in which an intermediate C-atom carries the two halogen atoms. As these *ketone chlorides* readily exchange their chlorine for hydrogen, they constitute a means of converting the ketones into the corresponding paraffins.

12. The hydrogen atoms of the alkyl groups present in the ketones can be replaced by chlorine and bromine.

13. The lower members of the series of aldehydes showed a great tendency to polymerize, but no ketone has been known to do this. Ketones, in contrast to aldehydes, are symmetrically constructed.

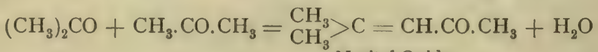
14. By the action of amyl nitrite and sodium ethylate or hydrochloric acid upon the ketones, isonitrosoketones result; these contain the CH or CH_2 groups, together with the CO-group.

Nucleus-synthetic Reactions of the Ketones.—Reactions of this class were observed in the action of ammonia and of phosphorus trichloride, in the presence of aluminium chloride, upon acetone (compare 9 and 10). The latter is capable of such deportment. The following are, however, more important:

(1) Just as two aldehyde molecules *condense* to *aldol*, so aldehyde or chloral will unite with acetone, forming *hydracetyl acetone* and *trichlorhydracetyl acetone* (see this):

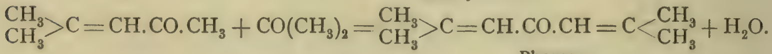
$$CH_3.C{\lessgtr}^{O}_{H} + CH_3.CO.CH_3 = CH_3.CH{<}^{OH}_{CH_2.CO.CH_3}.$$

Acetone will also condense with other aldehydes,—*e.g.*, benzaldehyde. But it is impossible to fix the ketone-alcohols which form at first. There is an exit of water, and unsaturated derivatives are produced, just as in the condensation of two molecules of aldehyde to *crotonaldehyde*. Thus, two molecules of acetone, in the presence of $ZnCl_2$, HCl, SO_4H_2, unite directly with the exit of water and the formation of *mesityl oxide* (p. 219), which in turn condenses with a third molecule of acetone to *phorone* (p. 219). The ketone alcohols, first formed, were not tangible:



$$(CH_3)_2CO + CH_3.CO.CH_3 = \genfrac{}{}{0pt}{}{CH_3}{CH_3}{>}C = CH.CO.CH_3 + H_2O$$

Mesityl Oxide



$$\genfrac{}{}{0pt}{}{CH_3}{CH_3}{>}C = CH.CO.CH_3 + CO(CH_3)_2 = \genfrac{}{}{0pt}{}{CH_3}{CH_3}{>}C = CH.CO.CH = C{<}\genfrac{}{}{0pt}{}{CH_3}{CH_3} + H_2O.$$

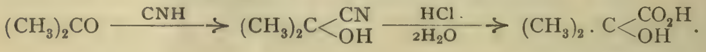
Phorone.

(2) Acetone and other ketones, having a suitable constitution, pass over, under the influence of concentrated sulphuric acid, into symmetrical trialkyl benzenes. It is very probable that there is an intermediate formation of alkylized acetylenes (p. 98). Acetone yields *mesitylene*:

Acetone Allylene Mesitylene.

(3) Acetone condenses with lime or sodium ethylate to *isophorone*, a trimethyl oxo-cyclo-hexene (see this).

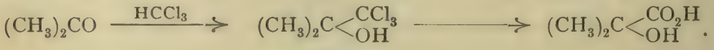
(4) The ketones, like the aldehydes, unite with hydrogen cyanide to form *oxycyanides* or *cyanhydrins*, the nitriles of the *a-oxyacids*. They will be described after the *a-oxyacids*, into which they pass when treated with hydrochloric acid:



$$(CH_3)_2CO \xrightarrow{CNH} (CH_3)_2C{<}\genfrac{}{}{0pt}{}{CN}{OH} \xrightarrow[2H_2O]{HCl} (CH_3)_2.C{<}\genfrac{}{}{0pt}{}{CO_2H}{OH}.$$

α-Oxyisobutyric Acid.

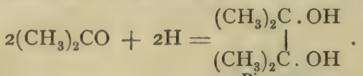
(5) Acetone in the presence of caustic soda combines with chloroform, yielding *acetone chloroform*. It is a derivative of α-oxyisobutyric acid. The latter can be obtained from it:



$$(CH_3)_2CO \xrightarrow{HCCl_3} (CH_3)_2C{<}\genfrac{}{}{0pt}{}{CCl_3}{OH} \longrightarrow (CH_3)_2C{<}\genfrac{}{}{0pt}{}{CO_2H}{OH}.$$

Acetone Chloroform α-Oxyisobutyric Acid.

(6) Nascent hydrogen converts the ketones not only into secondary alcohols (p. 113) but also into pinacones, or ditertiary glycols (p. 212):



$$2(CH_3)_2CO + 2H = \begin{array}{l}(CH_3)_2C.OH \\ \quad\;\; | \\ (CH_3)_2C.OH\end{array}.$$

Pinacone,
Tetramethyl Glycol.

Acetone, *Dimethyl ketone* [*Propanon*], $CH_3.CO.CH_3$, boiling at 56.5°, is isomeric with *propionic aldehyde*, *propylene oxide*, *trimethylene oxide*, and *allyl alcohol*. It occurs in small quantities in the blood and normal urine, while in the urine of those suffering from diabetes it is present in considerable amount, due, apparently, to the breaking down of the aceto-acetic acid formed at first. It is also produced in the dry distillation of *tartaric acid*, *citric acid* (see this), sugar, cellulose (wood), hence is found in crude wood spirit (p. 117). Technically it is prepared by the distillation of calcium acetate, or from crude wood spirit.

It is also formed: by the oxidation of isopropyl alcohol, isobutyric acid, and α-oxyisobutyric acid, by heating chloracetol and bromacetol, $CH_3CBr_2CH_3$, with water to 200°.

We would naturally expect an alcohol, $CH_3 . C(OH) : CH_2$, to be formed here, but a transposition of atoms occurs and acetone results (see p. 53). Acetone is similarly formed from allylene, $CH_3 . C \vdots CH$, by action of sulphuric acid or $HgBr_2$ in the presence of water (p. 98).

It results further in the action of zinc methide upon acetyl chloride; compare general methods for the preparation of ketones, page 210.

Acetone is a mobile, peculiar-smelling liquid, having a sp. gr. of 0.7920 at 20°. It is miscible with water, alcohol, and ether. Calcium chloride (or potash) sets it free from its aqueous solution.

It is an excellent solvent for many carbon compounds. Its most important reactions were described under the transformations of the ketones (p. 211), as well as its deportment toward nascent hydrogen, oxidizing agents, amyl nitrite, hydrogen sulphide, mercaptans and hydrochloric acid, alkali bisulphites, ammonia, hydroxylamine, phenylhydrazine, phosphorus pentachloride, halogens, condensation agents, hydrocyanic acid, chloroform, and caustic potash. See β-allyl alcohol, page 131, for the action of sodium upon acetone.

Acetone is used in the preparation of *sulphonal* (p. 218), *chloroform* (p. 234), and *iodoform* (p. 235). The production of iodoform serves for the detection of acetone (B. **13**, 1002; **14**, 1948; **17**, R. 503; **29**, R. 1006). For other reactions answering for its detection, consult B. **17**, R. 503; **18**, R. 195; A. **223**, 143.

Cycloacetone Superoxide, $(C_3H_6O_2)_3$, melting at 97°, is produced by the interaction of equimolecular quantities of acetone and hydrogen peroxide in concentrated solution. It crystallizes beautifully, is insoluble in water, but dissolves readily in benzene and in ether. It explodes when struck or when heated (Ch. Ztg. 1896, I, 156).

Homologues of Acetone.—(*a*) *Simple Ketones.* Usually prepared by the distillation of the calcium or barium salts of the corresponding acids.

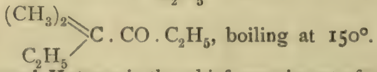
Name.	Formula.	M. P.	B. P.
Diethyl Ketone, *Propione* [3-Pentanon],	$CO(C_2H_5)_2$	—	103°
Di-n-Propyl Ketone, Butyron,	$CO(C_3H_7)_2$	—	144°
Di-isopropyl Ketone, *Tetramethyl Acetone*,	$CO[CH(CH_3)_2]_2$	—	124°
n-Caprone,	$CO(C_5H_{11})_2$	14.6°	226°
Tetra-ethyl Acetone,	$CO[CH(C_2H_5)_2]_2$	—	203°
Oenanthone,	$CO(C_6H_{13})_2$	30°	263°
Caprylone,	$CO(C_7H_{15})_2$	40°	—
Caprinone,	$CO(C_8H_{17})_2$	48°	—
Laurone,	$CO(C_{11}H_{23})_2$	69°	—
Myristone,	$CO(C_{13}H_{27})_2$	76°	—
Palmitone,	$CO(C_{15}H_{31})_2$	83°	—
Stearone,	$CO(C_{17}H_{35})_2$	88°	—

Diethyl ketone is produced from carbon monoxide and potassium ethide (p. 184). Tetramethyl- and tetraethyl-acetone have been obtained as decomposition products of *penta-methyl* and *penta-ethyl phloroglucin*, when these bodies were oxidized by air (B. **25**, R. 504).

(*b*) *Mixed Ketones.* Most of the members of this class are made by the distillation of the barium salts of the corresponding acids with barium acetate (p. 209).

Name.	Formula.	M. P.	B. P.
Methyl Ethyl Ketone [Butanon], . .	$CH_3 . CO . C_2H_5$	—	81°
Methyl Propyl Ketone [2-Pentanon],	$CH_3 . CO . C_3H_7$	—	102°
Methyl Isopropyl Ketone [Methyl Butanon], ...	$CH_3 . CO . CH(CH_3)_2$	—	96°
Pinacoline, Methyl Tertiary Butyl Ketone, ...	$CH_3 . CO . C(CH_3)_3$	—	106°
Methyl Oenanthone, Methyl Hexyl Ketone, ...	$CH_3 . CO . C_6H_{13}$	—	171°
Methyl Nonyl Ketone, ...	$CH_3 . CO . C_9H_{19}$	+ 15°	225°
Methyl Decyl Ketone, ...	$CH_3 . CO . C_{10}H_{21}$	21°	247°
Methyl Undecyl Ketone from Lauric Acid, ...	$CH_3 . CO . C_{11}H_{23}$	28°	263°
Methyl Dodecyl Ketone, ...	$CH_3 . CO . C_{12}H_{25}$	34°	(207°)
Methyl Tridecyl Ketone from Myristic Acid, ...	$CH_3 . CO . C_{13}H_{27}$	39°	(224°)
Methyl Tetradecyl Ketone, ...	$CH_3 . CO . C_{14}H_{29}$	43°	(231°)
Methyl Pentadecyl Ketone from Palmitic Acid, ...	$CH_3 . CO . C_{15}H_{31}$	48°	(244°)
Methyl Hexadecyl Ketone from Margaric Acid, ...	$CH_3 . CO . C_{16}H_{33}$	52°	(252°)
Methyl Heptadecyl Ketone from Stearic Acid, ...	$CH_3 . CO . C_{17}H_{35}$.	55°	(265°)

The boiling points, inclosed in parentheses, were determined under 100 mm. pressure.

Pinacoline is obtained by the withdrawal of water from pinacone, called hexylene glycol, from tetramethyl glycol $(CH_3)_2C(OH) . C(OH)(CH_3)_2$, and from trimethyl acetyl chloride and zinc methide (p. 209). When oxidized with chromic acid, it breaks down into trimethyl acetic acid and formic acid. Potassium permanganate converts it into trimethyl pyroracemic acid (see this). Pinacolyl alcohol (p. 129) is the product of its reduction. *Homologous pinacones* yield homologous pinacolines; thus, *methyl ethyl pinacone*, $\begin{matrix}CH_3\\C_2H_5\end{matrix}\!>\!C(OH) . C(OH)\!<\!\begin{matrix}CH_3\\C_2H_5\end{matrix}$, yields *ethyl tertiary amyl ketone*, 
$\begin{matrix}(CH_3)_2\\C_2H_5\end{matrix}\!>\!C . CO . C_2H_5$, boiling at 150°.

Methyl-nonyl Ketone is the chief constituent of oil of rue (from *Ruta graveolens*); it may be extracted from this by shaking with primary sodium sulphite.

1. HALOGEN SUBSTITUTION PRODUCTS OF THE KETONES, PARTICULARLY ACETONE.

Monochloracetone, $CH_3 . CO . CH_2Cl$, boiling at 119°, is obtained by conducting chlorine into cold acetone (A. **279**, 313), in the presence of marble (B. **26**, 597). Its vapors provoke tears.

There are two possible **Dichloracetones**, $C_3H_4Cl_2O$: (a) $CH_3 . CO . CHCl_2$ and (β) $CH_2Cl . CO . CH_2Cl$. The first is formed on treating warmed acetone with chlorine, and is obtained from dichloraceto-acetic ester (B. **15**, 1165). It boils at 120°. The β-dichloracetone is obtained by the chlorination of acetone and in the oxidation of α-dichlorhydrin, $CH_2Cl . CH(OH) . CH_2Cl$ (see glycerol), with potassium dichromate and sulphuric acid. It melts at 45°, and boils at 172°–174°.

Symmetrical **Tetrachloracetone,** $CHCl_2 . CO . CHCl_2 + 2H_2O$, is readily obtained by the action of potassium chlorate and hydrochloric acid upon chloranilic acid (B. **21**, 318) and triamidophenol (B. **22**, R. 666), or of chlorine upon phloroglucin (B. **22**, 1478). It melts at 48°. Unsymmetrical *Tetrachloracetone*, $CH_2Cl . CO . CCl_3$, boiling at 183°, is produced by the action of chlorine upon isopropyl alcohol (B. **28**, R. 61). **Pentachloracetone,** $CHCl_2 . CO . CCl_3$, boiling at 193°, is obtained from chlorine and acetone (A. **279**, 317).

Monobromacetone, $CH_2Br . CO . CH_3$, boils at 31° (8 mm.) (B. **29**, 1555). **Perbromacetone,** $CBr_3 . CO . CBr_3$, melting at 110°–111°, is obtained from triamidophenol (B. **10**, 1147), and bromanilic acid (B. **20**, 2040; **21**, 2441) by means of bromine and water.

Iodoacetone, $CH_3 . CO . CH_2I$, boiling at 58° (11 mm.) is produced when potassium iodide in methyl alcohol solution acts upon mono-chloracetone (B. **29**, 1557). It is a heavy oil with a disagreeable odor (B. **18**, R. 330).

β-**Di-iodoacetone,** $CH_2I . CO . CH_2I$, forms when iodine chloride acts upon acetone.

β-Chlorisobutyl-methyl Ketone, $(CH_3)_2 . CCl . CH_2 . CO . CH_3$, and *Di-$\beta$-chlorisobutyl Ketone*, $(CH_3)_2CCl . CH_2 . CO . CH_2CCl(CH_3)_2$, are the readily decomposable addition products of *mesityl oxide* and *phorone* with hydrochloric acid. *ω-Brombutyl-methyl Ketone*, see Acetobutyl alcohol.

γ-Dibrom-ketones are prepared from the *oxetones* (see these) by the addition of 2HBr, *e.g.: γ-Dibrombutyl Ketone*, $(CH_3CHBr . CH_2 . CH_2)_2CO$, is formed from dimethyl oxetone and 2HBr, or by the addition of 2HBr to diallyl acetone (p. 221). *α-Dichlor-ketones* are discussed with the diketones.

2. ALKYL ETHERS OF THE ORTHO-KETONES.

The ketones may be regarded as the anhydrides of hypothetical glycols, which bear the same relation to the ketones that the orthocarbonic acids sustain to the carbonic acids. In this sense it is then permissible to speak of ortho-ketones. Their alkyl ethers, corresponding to the acetals, are produced by heating the β-diethoxy-carbonic acids, and also from acetone by means of orthoformic ester (Claisen, B. **29**, 1007):

$$CH_3 . C(O . C_2H_5)_2CH_2 . CO_2H \longrightarrow CH_3 . C(O . C_2H_5)_2 . CH_3 + CO_2$$
$$CH_3 . CO . CH_3 + HC(O . C_2H_5)_3 \longrightarrow CH_3 . C(O . C_2H_5)_2CH_3 + HCO_2C_2H_5.$$

Ortho-acetone Methyl Ether, $(CH_3)_2C(O . CH_3)_2$, boils at 83°. *Ortho-acetone Ethyl Ether*, boiling at 114°, is a liquid with an odor resembling that of camphor. These substances are stable when alone. Water or a trace of mineral acid causes them to break down into ketones and alcohols.

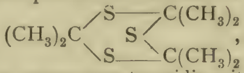
3. KETONE HALOIDS

Are produced, as mentioned on page 213, by the action of PCl_5, PCl_3Br_2, and PBr_5 upon ketones.

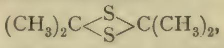
Acetone chloride, *Chloracetol*, $CH_3 . CCl_2 . CH_3$, boils at 70°; sp. gr. 1.827 at 16°. *Bromacetol* boils at 114°; sp. gr. 1.8149 (0°). **Methyl-ethyl dichlormethane,** $CH_3 . CCl_2 . C_2H_5$, boils at 96°. **Methyl-ethyl dibrommethane** boils at 144°. **Methyl tertiary butyl dichlormethane,** $CH_3 . CCl_2 . C(CH_3)_3$, boils at 151°.

4. SULPHUR DERIVATIVES OF THE PARAFFIN KETONES.

A. **Thioketones and their Sulphones.**—When hydrogen sulphide acts upon a cold mixture of acetone and concentrated hydrochloric acid, the first product is a volatile body with an exceedingly disagreeable odor, which disseminates itself astonishingly rapidly. It is probably simple thio-acetone, which has not been further investigated. The final product of the reaction is—

Trithioacetone, , melting at 24°, and boiling at 130° (13 mm.). Potassium permanganate oxidizes it to—

Trisulphone Acetone, $[(CH_3)_2CSO_2]_3$, melting at 302°. When distilled at the ordinary pressure it is converted into

Dithioacetone,  $(CH_3)_2C<^{S}_{S}>C(CH_3)_2$, boiling at 183–185°. This is also formed in the action of phosphorus trisulphide upon acetone. It is converted, by oxidation, into—

Disulphone Acetone, $[(CH_3)_2CSO_2]_2$, melting at 220–225°.

B. **Mercaptols and their Sulphones.**—Although the ketone derivatives corresponding to the *acetals* can not be derived from ketones and alcohols by the withdrawal of water, it is possible to obtain the *mercaptols*—the ketone derivatives corresponding to the *mercaptals*—in this manner, but best, however, by the action of hydrochloric acid upon ketones and mercaptans:

$$(CH_3)_2CO + 2C_2H_5SH \xrightarrow{HCl} (CH_3)_2C(SC_2H_5)_2 + H_2O.$$

Like the mercaptals, they are liquids with unpleasant odor.

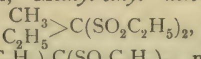
Acetone Ethyl Mercaptol, *Dithioethyl dimethyl methane*, $(CH_3)_2C(SC_2H_5)_2$, boiling at 190–191°, may be prepared from mercaptan. However, to avoid the very intolerable odor of the latter, sodium ethyl thiosulphate and hydrochloric acid are used (p. 153). It combines with methyl iodide (B. **19**, 1787; **22**, 2592). By this means, from a series of simple and mixed ketones, corresponding mercaptols have been made, and in nearly all instances they have been oxidized to the corresponding sulphones, some of which possess medicinal value.

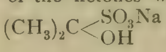
Sulphonal, *Acetone Diethyl Sulphone*, $(CH_3)_2C(SO_2C_2H_5)_2$, melting at 126°, was discovered by Baumann, and introduced into medicine, as a very active sleep-producing agent, by Kast in 1888. Acetone mercaptol is oxidized to it by potassium permanganate:

$$(CH_3)_2 . C(SC_2H_5)_2 \xrightarrow{4O} (CH_3)_2C(SO_2C_2H_5)_2.$$

Sodium hydroxide and methyl iodide (A. **253**, 147) acting upon *ethidene diethyl sulphone* (p. 204) produce it:

$$CH_3CH(SO_2C_2H_5)_2 \xrightarrow{NaOH} CH_3 . CNa(SO_2C_2H_5)_2 \xrightarrow{CH_3I} (CH_3)_2C(SO_2C_2H_5)_2.$$

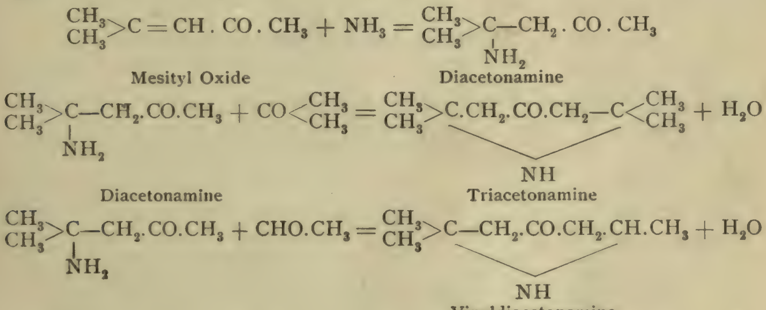
Trional, *Methyl-ethyl ketone-diethyl sulphone, diethyl-sulphone-methyl-ethyl-methane*,  $^{CH_3}_{C_2H_5}>C(SO_2C_2H_5)_2$, melting at 75°; **Tetronal,** *Propione-diethyl sulphone*, $(C_2H_5)_2C(SO_2C_2H_5)_2$, melting at 85°; **Propione-dimethyl Sulphone,** $(C_2H_5)_2C(SO_2CH_3)_2$, melting at 132°–133°, and other "*sulphonals*," are prepared similarly to *sulphonal*, and act in like manner. However, **Acetone-dimethyl Sulphone,** $(CH_3)_2C(SO_2CH_3)_2$, not containing an ethyl group, no longer acts like sulphonal.

C. **Oxysulphonic Acids of the Ketones.**—The alkali salts of these acids are the addition compounds produced by the union of the ketones with the alkaline bisulphites, *e. g.*, sodium acetone-oxysulphonate,  $(CH_3)_2C<^{SO_3Na}_{OH}$ (p. 213).

5. NITROGEN DERIVATIVES OF THE KETONES.

A. **Nitro-compounds.**—*Pseudonitrols* (p. 157) and *Mesodinitroparaffins* (p. 158) have already been discussed after the mononitroparaffins.

B. **Ammonia and Acetone** (Heintz, A. 174, 133; 198, 42).—Two bases result from the action of ammonia upon acetone: **diacetonamine** and **triacetonamine.** It may be supposed that the ammonia causes the acetone to condense, just as the alkalies and alkaline earths do, and that acetone ammonia, an intermediate product, combines with the ammonia, or ammonia with *mesityl oxide*, to yield diacetonamine, which by further treatment with acetone is changed to triacetonamine, or when acted upon by aldehydes passes into vinyldiacetonamine (B. 17, 1788), or into a δ-lactam through the agency of cyanacetic ester (B. **26**, R. 450):



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>C=CH.CO.CH_3+NH_3=\begin{matrix}CH_3\\CH_3\end{matrix}\!>\underset{\displaystyle NH_2}{\underset{|}{C}}-CH_2.CO.CH_3$$

Mesityl Oxide Diacetonamine

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>\underset{\displaystyle NH_2}{\underset{|}{C}}-CH_2.CO.CH_3+CO<\begin{matrix}CH_3\\CH_3\end{matrix}=\begin{matrix}CH_3\\CH_3\end{matrix}\!>\underbrace{C.CH_2.CO.CH_2-C}_{NH}<\begin{matrix}CH_3\\CH_3\end{matrix}+H_2O$$

Diacetonamine Triacetonamine

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>\underset{\displaystyle NH_2}{\underset{|}{C}}-CH_2.CO.CH_3+CHO.CH_3=\begin{matrix}CH_3\\CH_3\end{matrix}\!>\underbrace{C-CH_2.CO.CH_2.CH}_{NH}.CH_3+H_2O$$

Vinyldiacetonamine.

Diacetonamine is a colorless liquid, not very soluble in water. When distilled it decomposes into mesityl oxide and NH_3; conversely, mesityl oxide and NH_3 combine to form diacetonamine (B. 7, 1387). It reacts strongly alkaline and is an amide base, forming crystalline salts with one equivalent of acid. If potassium nitrite be allowed to act on the HCl-salt, *diacetone alcohol*, $(CH_3)_2C(OH).CH_2.CO.CH_3$, results; this loses water and becomes mesityl oxide. For the urea derivatives of acetone, consult B. **27**, 377.

A chromic acid mixture oxidizes diacetonamine to amidoisobutyric acid, $(CH_3)_2.C(NH_2).CO_2H$ (Propalanine), and amidoisovaleric acid, $(CH_3)_2C(NH_2)CH_2.CO_2H$.

Triacetonamine crystallizes in anhydrous needles, melting at 39.6°. With one molecule of water it forms large quadratic plates, fusing at 58°. It is an imide base (p. 167) with feeble alkaline reaction; potassium nitrite converts its HCl-salt into the nitroso-amine compound, $C_9H_{16}(NO)NO$, which fuses at 73° and passes into phorone when boiled with caustic soda. Hydrochloric acid regenerates triacetonamine from the nitroso-derivative.

By the addition of 2H to triacetonamine, converting the CO group into CH . OH, there results an *alkamine*, $C_9H_{19}NO$, which may be viewed as hydroxy-tetramethyl piperidine. By the abstraction of water from this, the base $C_9H_{17}N$, triacetonine, boiling at 146°, results. This approaches tropidine, $C_8H_{13}N$, very closely (B. **16**, 2236; **17**, 1788).

n-*Methyl-triacetonamine* and allied bases (B. **28**, R. 160) are formed when phorone is treated with primary amines.

C. **Ketoximes** (V. Meyer).—In general, the ketoximes are formed with greater difficulty than the aldoximes. It is usually best to apply the hydroxylamine in a strongly alkaline solution (B. **22**, 605; A. **241**, 187). They are also produced when the pseudonitriles are reduced by free hydroxylamine or potassium sulphydrate (B. **28**, 1367; **29**, 87, 98). They are very similar in properties to the aldoximes. Acids resolve them into their components, while sodium amalgam and acetic acid convert them into *primary amines* (p. 161). They are characteristically distinguished from the aldoximes by their deportment toward acid chlorides or acetic anhydride, yielding in part acid esters, and, again, by the same reagents, as well as by HCl in glacial acetic acid, being changed to acid amides (Beckmann's transposition, B. **20**, 506, 2580; compare also B. **24**, 4018):

$$\mathrm{CH_3\,.\,CH_2\,.\,CH_2}\!\!\overset{\mathrm{CH_3}}{>}\!\mathrm{CH = NOH} \longrightarrow \mathrm{CH_3\,.\,CO\,.\,NHCH_2\,.\,CH_2\,.\,CH_3}.$$

Methyl Propyl Ketoxime Acetpropylamide.

Nitrogen tetroxide converts the ketoximes into *pseudonitrols* (p. 158).

Ketoximes combine with hydrocyanic acid to form nitriles of α-amidoxyl carboxylic acids (B. **29**, 62).

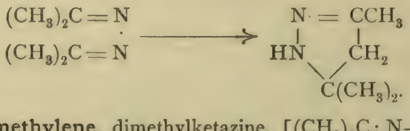
Acetoxime, $(CH_3)_2C:NOH$, melting at 59–60° and boiling at 135°, smells like chloral. It dissolves readily in water, alcohol, and ether (B. **20**, 1505).

Hypochlorous acid converts acetoxime into *hypochlorous ester*, $(CH_3)_2C:N.OCl$, a liquid with an agreeable odor. It boils at 134°. It explodes, however, when rapidly heated (B. **20**, 1505).

The hydroxyl hydrogen present in acetoxime may be replaced by acid radicals through the agency of acid chlorides or anhydrides (B. **24**, 3537). With sodium alcoholate, the sodium derivative results, which yields the alkyl ethers, $(CH_3)_2C:N.OR$, when acted upon by the alkylogens. On boiling these ethers with acids, acetone and alkylized hydroxylamines, NH_2OR (B. **16**, 170), are produced. The higher acetoximes show a perfectly analogous deportment.

Methyl-ethyl-ketoxime boils at 152–153°. **Methyl-n-propyl Ketoxime** is an oil with agreeable odor. **Methyl-isopropyl Ketoxime** boils at 157–158°. *Methyl-n-butyl Ketoxime* boils at 185°. *Methyl tertiary butyl Ketoxime* melts at 74–75°. n-*Butyronoxime* boils at 190–195°. *Isobutyronoxime* melts at 6–8° and boils at 181–185°. *Methylnonyl Ketoxime* melts at 42°. *Caprylonoxime* melts at 20°. *Nonyloxime* melts at 12°. *Lauronoxime*, $(C_{11}H_{23})_2C:N.OH$, melts at 39–40°. *Myristonoxime*, $(C_{13}H_{27})_2C:N.OH$, melts at 51°. **Palmitonoxime**, $(C_{15}H_{31})_2C:N.OH$, melts at 59°. *Stearonoxime*, $(C_{17}H_{35})_2C:N.OH$, melts at 62–63°.

D. **Ketazines** (Curtius and Thun).—An excess of hydrazine acting upon the ketones produces the unstable, secondary unsymmetrical hydrazines, which even in the cold readily become ketazines, quite stable toward alkalies (B. **25**, R. 80). Dimethylketazine in contact with maleic acid changes to the isomeric trimethyl pyrazoline (B. **27**, 770):



Bisdimethylazimethylene, dimethylketazine, $[(CH_3)_2C:N—]_2$, boils at 131°; **Bismethylethylazimethylene** boils at 168–172°; **Bismethylpropylazimethylene** boils at 195–200°; **Bismethylhexylazimethylene** boils at 290°; **Bisdiethylazimethylene** boils at 190–195°.

E. **Ketone-phenylhydrazones** (E. Fischer, B. **16**, 661; **17**, 576; **20**, 513; **21**, 984).—These compounds result by the action of phenylhydrazine upon the ketones. The phenylhydrazine is added to the ketone until a sample of the mixture no longer reduces an alkaline copper solution. They behave like the aldehyde phenylhydrazones (p. 207).

Acetone-phenylhydrazone, $(CH_3)_2C:N_2HC_6H_5$, melts at 16° and boils at 165° (91 mm.).

Methyl-n-propylketone-phenylhydrazone, $(CH_3)(C_3H_7)C:N_2HC_6H_5$, boils at 205–208° (100 mm.).

3 B. OLEFINE AND DIOLEFINE KETONES.

Such bodies have been obtained by the direct condensation of acetone: *mesityl oxide* and *phorone* (p. 214). They have also resulted from 1,3-ketone alcohols by the elimination of water.

Ethidene Acetone, $CH_3CH=CH.CO.CH_3$, boils at 122°. It has a penetrating odor like that of crotonaldehyde. It is formed when *hydracetylacetone* (see this) is boiled with acetic anhydride (B. 25, 3166). **Heptachlorethidene Acetone**, $CHCl_2CCl=CCl.CO.CCl_3$, boils at 182–185° (13–15 mm.). It results when *trichloracetyl tetrachloracetone* is heated with water (B. 25, 2695).

Mesityl Oxide, $(CH_3)_2C=CH.CO.CH_3$, boiling at 130°, is a liquid smelling like peppermint. **Phorone**, $(CH_3)_2C=CH.CO.CH=C(CH_3)_2$, melts at 28° and boils at 196°. These are formed simultaneously on treating acetone with dehydrating agents, *e.g.*, $ZnCl_2$, H_2SO_4, and HCl. Hydrochloric acid is best adapted for this purpose, the acetone being saturated with it, while it is cooled. The hydrochloric acid addition products, $(CH_3)_2CCl.CH_2.COCH_3$ and $(CH_3)_2CCl.CH_2.CO.CH_2.CCl(CH_3)_2$, are decomposed by caustic alkalies, and the mesityl oxide and phorone then separated by distillation. When acetone is condensed by lime or sodium ethylate there is produced along with the mesityl oxide a cyclic ketone isomeric with phorone. It is called **isophorone**. **Camphor-phorone** is also isomeric with these two phorones. Mesityl oxide combines with ammonia to diacetonamine (p. 219), and with hydrazine to trimethyl pyrazoline. Mesityl oxide is also produced when *diacetone alcohol* (see this) and *diacetonamine* (p. 219) are heated alone; also together with acetone when phorone is heated with dilute sulphuric acid, which eventually causes it to break down into *two* molecules of acetone, as the result of water absorption (A. 180, 1); also by the action of isobutylene upon acetic anhydride in the presence of a little $ZnCl_2$ (B. 27, R. 942). Mesityl oxide takes up two and phorone four bromine atoms; both yield oximes with hydroxylamine.

Historical.—Kane discovered mesityl oxide in 1838, when he obtained it, together with mesitylene, by the action of concentrated sulphuric acid on acetone. At that time he regarded acetone as alcohol, and called it *mesitalcohol*. In mesityl oxide and mesitylene, Kane thought he had discovered bodies which bore the same relation to mesityl alcohol or acetone that ethyl ether or ethyl oxide and ethylene bore to ethyl alcohol. Kekulé developed the formula $(CH_3)_2.C=CH.CO.CH_3$ for mesityl oxide, which had been suggested by Claisen. Baeyer discovered phorone, and Claisen assigned to it the formula $(CH_3)_2C=CH.CO.CH=C(CH_3)_2$ (A. 180, 1).

Methylheptenone, $(CH_3)_2C=CH.CH_2.CH_2.CO.CH_3$, boiling at 173°, occurs in many ethereal oils, *e.g.*, citral, geranium oil, etc. It is produced in the distillation of cineolic anhydride. It has been synthesized by treating the reaction-product resulting from sodium acetonylacetone and amylene dibromide, $(CH_3)_2CBr.CH_2.CH_2Br$, with caustic soda (B. 29, R. 590). It is a liquid with a penetrating odor resembling that of amyl acetate. Potassium permanganate decomposes it into acetone and lævulinic acid. Zinc chloride converts it into m-dihydroxylene (A. 258, 323; B. 28, 2115, 2126). *Isoamylidene acetone*, $(CH_3)_2CH.CH_2.CH=CH-COCH_3$, boils at 180° (B. 27, R. 121).

Diallylacetone, $CH_2=CH.CH_2.CH_2.CO.CH_2.CH_2.CH=CH_2$, boiling at 116° (70 mm.), is obtained from diallyl-acetone dicarboxylic ester (compare oxetones).

Pseudoionone is a diolefine-ketone, and it will be described together with the olefine terpenes.

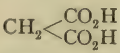
4. MONOBASIC ACIDS.

The organic acids are characterized by the atomic group, $CO.OH$, called *carboxyl*. The hydrogen of this can be replaced by metals and alcohol radicals, forming salts and esters. These organic acids may be compared to the sulphonic acids, containing the sulpho-group, $SO_2.OH$.

The number of carboxyl groups present in them determines their basicity, and distinguishes them as mono-, di-, tri-basic, etc., or as mono-, di- and tri-carboxylic acids:

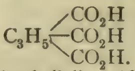
$CH_3.CO_2H$

Acetic Acid (Monobasic)



$$CH_2<\begin{matrix}CO_2H\\CO_2H\end{matrix}$$

Malonic Acid (Dibasic)



$$C_3H_5\begin{matrix}\diagup CO_2H\\ -CO_2H\\ \diagdown CO_2H.\end{matrix}$$

Tricarballylic Acid. (Tribasic).

We can view the monobasic *saturated* acids as combinations of the carboxyl group with alcohol radicals; they are ordinarily termed *fatty acids*. They correspond to the saturated primary alcohols and aldehydes. The *unsaturated* acids of the acrylic acid and propiolic acid series, corresponding to the unsaturated primary alcohols and aldehydes, are derived from the fatty acids by the exit of two and four hydrogen atoms.

They are distinguished as:

A. Paraffin monocarboxylic Acids, $C_nH_{2n}O_2$, formic acid or acetic acid series.

B. Olefine monocarboxylic Acids, $C_nH_{2n-2}O_2$, oleic or acrylic acid series.

C. Acetylene monocarboxylic Acids, $C_nH_{2n-4}O_2$, propiolic acid series.

D. Diolefine carboxylic Acids, $C_nH_{2n-4}O_2$.

Nomenclature.—The "Geneva nomenclature" deduces the names of the carboxylic acids, just like the alcohols (p. 111), the aldehydes (p. 190), and the ketones (p. 211), from the corresponding hydrocarbons; thus formic acid is [methanic acid] and acetic acid is [ethanic acid], etc.

The *radical* of the acid is the residue in combination with the hydroxyl group:

$CH_3.CO—$ Acetyl

$CH_3.CH_2.CO—$ Propionyl

$CH_3.CH_2.CH_2.CO—$ Butyryl.

The names of the trivalent hydrocarbon residues, which in the acid residues are united with oxygen, are indicated by the insertion of the syllable "en" into the names of the corresponding alcohol radicals:

$CH_3.C\equiv$ Ethenyl

$CH_3.CH_2.C\equiv$ Propenyl

$CH_3.CH_2.CH_2.C\equiv$ n-Butenyl.

The group $CH\equiv$, however, is not only called the methenyl group, but also the methine group.

Review of the Derivatives of the Monocarboxylic Acids.—Numerous classes of bodies can be derived by changes in the carboxyl group. In connection with the fatty acids mention will only be made of the *salts*. The other classes of derivatives will be considered as such after the fatty acids. They are:

(1) The *esters*, resulting from the replacement of hydrogen in the carboxyl group by alcohol radicals (p. 253).

(2) The *chlorides* (bromides and iodides), which are compounds of the acid radicals with the halogens.

(3) The *acid anhydrides* (p. 259), compounds of the acid radicals with oxygen.

(4) The *acid peroxides* (p. 261).

(5) The *thio acids* (p. 261), compounds of the acid radicals with SH.

(6) The *acid amides* (p. 262), compounds of the acid radicals with NH_2.

(7) The *acid nitriles* (p. 266).

Hence acetic acid yields the following:

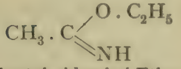
1. $CH_3 . CO_2 . C_2H_5$ Acetic Ethyl Ester
2. $CH_3 . COCl$ Acetyl Chloride
3. $(CH_3 . CO)_2O$ Acetic Anhydride
4. $(CH_3 . CO)_2O_2$ Acetyl Peroxide
5. $CH_3 . COSH$ Thiacetic Acid
6. $CH_3 . CONH_2$ Acetamide
7. $CH_3 . C{\equiv}N$ Acetonitrile.

Associated with the acid haloids, acid amides, and nitriles are: (8) *acid hydrazides* (p. 265); (9) *amide chlorides* (p. 268); (10) *imide chlorides* (p. 268); (11) *imido-ethers* (p. 269); (12) *thioamides* (p. 269); (13) *amidines* (p. 270); (14) *hydroxamic acids* (p. 270); (15) *nitrolic acids* (p. 270); (16) *amidoximes* (p. 271).

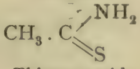
8. $CH_3 . CO . NH . NH_2$ Acetylhydrazine

9. $CH_3 . CCl_2 . NH_2$ Acetamide Chloride (unstable)

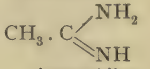
10. $CH_3 . CCl : NH$ Acetimide Chloride (unstable)

11. 
$CH_3 . C\begin{array}{l}\diagup O . C_2H_5\\ \diagdown NH\end{array}$

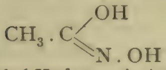
Acetoimidoethyl Ether

12. 
$CH_3 . C\begin{array}{l}\diagup NH_2\\ \diagdown S\end{array}$

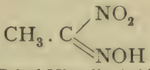
Thioacetamide

13. 
$CH_3 . C\begin{array}{l}\diagup NH_2\\ \diagdown NH\end{array}$

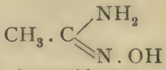
Acetamidine

14. 
$CH_3 . C\begin{array}{l}\diagup OH\\ \diagdown N . OH\end{array}$

Ethyl Hydroxamic Acid

15. 
$CH_3 . C\begin{array}{l}\diagup NO_2\\ \diagdown NOH\end{array}$

Ethyl Nitrolic Acid (p. 158)

16. 
$CH_3 . C\begin{array}{l}\diagup NH_2\\ \diagdown N . OH\end{array}$

Acetamidoxime.

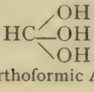
Numerous derivatives are also obtained by the replacement of the hydrogen atoms in the radical combined with hydroxyl by other atoms or groups. Only the *halogen substitution products* will be described under the fatty acids, after the discussion of the various classes mentioned in the preceding paragraphs.

The fatty acids can be recovered from all of the above classes of derivatives by simple reactions.

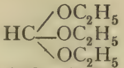
It has already been indicated, under the oxygen derivatives of the methane hydrocarbons, that aldehydes, ketones, and carboxylic acids may be considered as anhydrides of non-existing diacid or triacid alcohols, in which the hydroxyl groups are attached to the same carbon atom (p. 108). In this exposition the alcohols and ketones were especially recalled, because there were, for example, under the acetals (p. 200) and under the orthoketone alkyl ethers (p. 217), ethers of just such glycols or ortho-aldehydes, non-existent ordinarily in the free state, and of orthoketones, while chloral hydrate itself was such a glycol.

The trihydric alcohols, corresponding to the carboxylic acids, can not exist, but ethers of them are known. The hypothetical, trihydric alcohols, of which the carbonic acids may be considered anhydrides, have been called *ortho acids*, suggesting tribasic phosphoric acid as *orthophosphoric acid* (A. **139**, 114; J. (1859) 152; B. **2**, 115). This designation has also been conveyed to the orthoaldehydes and orthoketones.

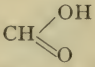
It is customary to speak of "hypothetical orthoformic acid" and of "orthoformic esters," the esters of tribasic formic acid, of *formic acid*,—which, in reference to the relation of orthophosphoric to metaphosphoric acid, PO(OOH), might be termed *metaformic acid*,—and of *formic acid esters*:



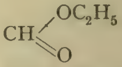
Orthoformic Acid



Orthoformic Ethyl Ester



Formic Acid



Formic Ethyl Ester.

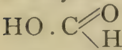
The *chloride*, *bromide*, and *iodide* corresponding to orthoformic acid are *chloroform*, *bromoform*, and *iodoform*.

It is only in the case of formic acid that the *ortho-acid derivatives* require a special designation. They will be discussed immediately following the derivatives of the ordinary formic acid.

A. MONOBASIC SATURATED ACIDS, PARAFFIN MONOCARBOXYLIC ACIDS,

$C_nH_{2n+1}.CO_2H$.

Formic acid, H.COOH, is the first member of this series. The radical HCO, in union with hydroxyl, is called *formyl*. This acid is distinguished from all its homologues and the unsaturated monocarboxylic acids, in that it manifests not only the character of a monobasic acid, but also that of an aldehyde. To express in a name its aldehyde character the acid might be designated *oxyformaldehyde*,



$HO.C\begin{smallmatrix}{=}O\\ {-}H\end{smallmatrix}$.

From a chemical standpoint, this acid stands closer to *glyoxylic acid*, CHO.CO_2H (see this) than to acetic acid. Therefore, formic acid and its derivatives will be treated before acetic acid and its homologues are discussed.

FORMIC ACID AND ITS DERIVATIVES.

It is not only the aldehyde character which distinguishes formic acid from acetic acid and its homologues, but it is also the absence of a chloride and anhydride, corresponding to acetyl chloride (see this) and acetic anhydride (see this). The withdrawal of water from formic acid leads to the formation of carbon monoxide; this is a transformation manifested by none of the higher homologues. Prussic acid (hydrocyanic acid), the nitrile of formic acid, has an acid nature, and therein differs from the indifferent nitriles of the homologous acids. Formic acid is twelve times stronger than acetic acid. The affinity constants from the electric conductivity show this (Ostwald).

To formic acid will be appended *carbon monoxide*, and its nitrogen-containing derivatives, the *isonitriles* or *carbylamines*, $C{=}N-R'$, and *fulminic acid*.

Formic Acid, HCO . OH (*Acidum formicum*), is found free in ants, in the case-worm of *Bombyx processionea*, in stinging nettles, in shoots of the pine, in various animal secretions (perspiration), and may be obtained from these substances by distilling them with water. It is produced artificially according to the usual methods:

(1) By the oxidation of methyl alcohol and formaldehyde:

$$H.CH_2OH \xrightarrow{O} H.CHO \xrightarrow{O} H.CO_2H.$$

(2) By heating hydrocyanic acid with alkalies or acids:

$$HCN + 2H_2O = HCO.OH + NH_3.$$

(3) By boiling chloroform with alcoholic potash (Dumas):

$$CHCl_3 + 4KOH = HCO.OK + 3KCl + 2H_2O.$$

(4) From chloral and (5) from propargylic aldehyde (p. 209) and caustic potash (Liebig):

$$CCl_3.CHO + NaOH = HCOONa + HCCl_3.$$

Worthy of mention is (6) the direct production of formates by the action of CO upon concentrated potash at 100°. The reaction occurs more easily if soda-lime at 200°–220° (Berthelot, A. **97**, 125; Geuther, A. **202**, 317; Merz and Tibiriçá, B. **13**, 718) be employed:

$$CO + NaOH = HCO.ONa.$$

(7) By action of acids upon isocyanides or carbylamines (p. 237):

$$CN.C_2H_5 + 2H_2O = H.CO_2H + C_2H_5NH_2.$$

(8) From fulminic acid by means of concentrated hydrochloric acid (see formyl chloridoxime, p. 233). Hydroxylamine is formed simultaneously:

$$C = N.OH + 2H_2O + HCl = H.CO_2H + NH_2OH.HCl.$$

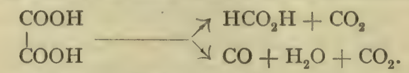
(9) By letting moist carbon dioxide act upon potassium:

$$3CO_2 + 4K + H_2O = 2HCO.OK + CO_3K_2$$ (Kolbe and Schmitt, A. **119**, 251).

Formates are also produced in the action of sodium amalgam upon a concentrated aqueous ammonium carbonate solution, or with the same reagent upon aqueous primary carbonates; likewise on boiling zinc carbonate with caustic potash and zinc dust.

(10) The most practical method of preparing formic acid consists in heating oxalic acid. This decomposition is accelerated by the presence of glycerol (Berthelot).

Oxalic acid treated alone decomposes into carbon dioxide and formic acid, or carbon monoxide and water; the latter decomposition preponderates:



$$\begin{array}{l} \text{COOH} \\ | \\ \text{COOH} \end{array} \longrightarrow \begin{cases} \nearrow HCO_2H + CO_2 \\ \searrow CO + H_2O + CO_2. \end{cases}$$

When, however, $(C_2O_4H_2 + 2H_2O)$ is added to moist concentrated glycerol and the whole heated to 100–110°, oxalic acid parts with its water of crystallization and unites with the glycerol to form *glycerol formic ester:*

$$C_3H_5\left\{\begin{array}{l} OH \\ OH \\ OH \end{array}\right. + C_2O_4H_2 = C_3H_5\left\{\begin{array}{l} OH \\ OH \\ O.COH \end{array}\right. + CO_2 + H_2O.$$

On further addition of crystallized oxalic acid the latter again breaks up into anhydrous acid and water, which converts the glycerol formic ester into glycerol and formic acid:

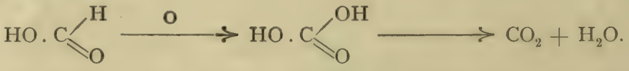
$$C_3H_5(OH)_2.(O.CHO) + H_2O = C_3H_5(OH)_3 + CHO.OH.$$

At first the acid is very dilute, but later it reaches 56 per cent. If anhydrous acid be employed at the beginning, a 95–98 per cent. formic acid is produced.

To obtain anhydrous acid, the aqueous product is boiled with lead oxide or lead carbonate. The lead formate is then decomposed, at 100°, by a current of hydrogen sulphide. Or, formic acid of high percentage is dehydrated by means of boric acid (B. 14, 1709).

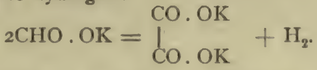
Formic acid is a mobile liquid with a specific gravity of 1.22 at 20° and boils at 100.6° (760 mm.). It becomes crystalline at 0°, and fuses at + 8.6°. It has a pungent odor and causes blisters on the skin. It mixes in all proportions with water, alcohol and ether, and yields the hydrate $4CH_2O_2 + 3H_2O$, which boils at 107.1° (760 mm.) and dissociates into formic acid and water. Concentrated, hot sulphuric acid decomposes formic acid into *carbon monoxide* and water. A temperature of 160° suffices to break up the acid into carbon dioxide and hydrogen. The same change may occur at ordinary temperatures by the action of pulverulent rhodium, iridium and ruthenium, but less readily when platinum sponge is employed.

According to its structure formic acid is also an aldehyde, as it contains the group CHO; this would account for its reducing property, its ability to precipitate silver from a hot neutral solution of silver nitrate, and mercury from mercuric nitrate, the acid itself oxidizing to *carbon dioxide:*



Formates, excepting the sparingly soluble lead and silver salts, are readily soluble in water. *Lead formate*, $(HCO_2)_2Pb$, crystallizes in beautiful needles and dissolves in 36 parts of cold water. *Silver formate*, HCO_2Ag, rapidly blackens on exposure to light.

Decomposition of Formates.—1. The alkali salts, heated carefully to 250°, become oxalates with evolution of hydrogen:



$$2CHO\,.\,OK = \begin{array}{l} CO\,.\,OK \\ | \\ CO\,.\,OK \end{array} + H_2.$$

2. By ignition of potassium formate with an excess of alkali it decomposes with the formation of a carbonate and the liberation of *pure hydrogen*, $H\,.\,CO_2K + KOH = K_2CO_3 + H_2$.

3. The ammonium salt, heated to 230°, passes into *formamide:*

$$H\,.\,CO_2NH_4 \xrightarrow[230^\circ]{-H_2O} H.CONH_2.$$

4. The silver salt and mercury salt, when heated, decompose into *metal*, carbon dioxide and formic acid:

$$2CHO_2Ag = 2Ag + CO_2 + H\,.\,CO_2H.$$

5. The *calcium* salt, when heated with the calcium salts of higher fatty acids, yields *aldehydes* (p. 188).

Monochlorformic acid, $CClO\,.\,OH$, is regarded as chlor-carbonic acid. It will be discussed after carbonic acid.

Esters of Formic Acid.—Liquids with an agreeable odor. They are prepared from (1) formic acid, alcohol and hydrochloric or sulphuric acid; (2) from sodium formate and alkyl sulphates; (3) from glycerol, oxalic acid and alcohols.

Methyl Formic Ester boils at 32.5°. **Perchlor-methyl formic ester,** $CClO_2\,.\,CCl_3$, boils at 180–185°. Heated to 305° it breaks up into carbonyl chloride, $C_2Cl_4O_2 = 2COCl_2$. Aluminium chloride converts it into CCl_4 and CO_2.

Ethyl Formic Ester boils at 54.4°.

This *ester* serves in the manufacture of artificial rum and arrack, and for the union of the formyl group with organic radicals (see formyl acetone, etc.).

The n-*propyl ester* boils at 81°. The n-*butyl ester* boils at 107°. For higher esters consult A. **233**, 253.

The *allyl ester* boils at 82–83°.

Formamide, $CHO\,.\,NH_2$, the *amide of formic acid* (compare acid amides) is obtained (1) by heating ammonium formate to 230° (B. **12**, 973; **15**, 980), or (2) ethyl formic ester with alcoholic ammonia to 100°; (3) by boiling formic acid with ammonium sulphocyanide (B. **16**, 2291). It is a liquid, readily soluble in water and alcohol, and boils with partial decomposition at 192°–195°. Heated rapidly it breaks up into CO and NH_3; P_2O_5 liberates HCN from it. It combines with chloral (p. 197) to form *chloral formamide*, $CCl_3\,.\,CH(OH)NHCHO$, melting at 114–115°, and finding use as a narcotic.

Mercuric oxide dissolves in it with the formation of mercury formamide, $(CHO\,.\,NH)_2Hg$. This is a feebly alkaline liquid, sometimes applied as a subcutaneous injection.

Ethyl Formamide, $CHO\,.\,NH\,.\,C_2H_5$, is obtained from ethyl formic ester; also by distilling a mixture of ethylamine with chloral:

$$CCl_3\,.\,CHO + NH_2\,.\,C_2H_5 = CHO\,.\,NH\,.\,C_2H_5 + CCl_3H.$$

It boils at 199°.

Allyl Formamide boils at 109° (15 mm.) (B. **28,** 1666).

Formyl Hydrazine, $HCONHNH_2$, melting at 54°, is obtained from formic ester and hydrazine. It yields triazole (B. **27,** R. 801) when heated with formamide.

Diformyl Hydrazine, HCONH . NH . COH, melting at 106°, is obtained from an excess of formic ester and hydrazine, heated to 130° (B. **28,** R. 242). Its lead salt and ethyl iodide yield *Diformyl Diethylhydrazine* (B. **27,** 2278).

Hydrocyanic Acid, *Prussic Acid, Formonitrile,* CNH, the *nitrile of formic acid* (see acid nitriles), is a powerful poison. It occurs free in an accumulated condition in all parts of the Java tree *Pangium edule* (B. **23,** 3548). It is obtained (1) from *amygdalin* (see this), a glucoside contained in bitter almonds, which, under favorable conditions, takes up water and breaks down into *prussic acid, grape sugar,* and *bitter almond-oil* or *benzaldehyde* (Liebig and Wöhler, A. **22,** 1). An aqueous solution, thus obtained, containing very little hydrocyanic acid, constitutes the officinal *aqua amygdalarum amararum;* its active ingredient is prussic acid. (2) By the action of phosphorus pentoxide upon formamide; (3) synthetically, by passing the electric spark through a mixture of acetylene and nitrogen (Berthelot); (4) from cyanogen and hydrogen under the influence of the silent electric discharge; (5) when chloroform is heated, under pressure, with ammonia; (6) upon boiling formoxime (p. 206) with water:

$$1.\ \underset{\text{Amygdalin}}{C_{20}H_{27}NO_{11}} + 2H_2O = CNH + \underset{\text{Benzaldehyde}}{C_6H_5CHO} + \underset{\text{Grape Sugar.}}{2C_6H_{12}O_6}$$

$$2.\ HCONH_2 \xrightarrow{P_2O_5} CNH + H_2O$$

$$3.\ CH{\equiv}CH + N_2 = 2CNH$$

$$4.\ CN.CN + H_2 = 2CNH$$

$$5.\ HCCl_3 + 5NH_3 = CNNH_4 + 3NH_4Cl$$

$$6.\ H_2C = N.OH = CNH + H_2O.$$

Hydrogen cyanide is prepared from metallic cyanides, particularly yellow prussiate of potash or potassium ferrocyanide, by the action of dilute sulphuric acid:

$$2Fe(CN)_6K_4 + 3SO_4H_2 = Fe_2(CN)_6K_2 + 3SO_4K_2 + 6CNH.$$

The aqueous prussic acid obtained in this way is dehydrated by distillation over calcium chloride or phosphorus pentoxide.

Historical.—Scheele discovered prussic acid in 1782. Gay-Lussac, in 1811, obtained it anhydrous, in the course of his memorable investigations upon the radical cyanogen. In hydrogen cyanide he recognized the hydrogen derivative of a radical, consisting of carbon and nitrogen, for which he suggested the name cyanogène (*κύανος, blue, γεννάω, to produce*).

Properties.—Anhydrous hydrocyanic acid is a mobile liquid, of specific gravity 0.697 at 18°, and becomes a crystalline solid at —15°. It boils at +26.5°. Its odor is peculiar, and resembles that of oil of bitter almonds. The acid is extremely poisonous.

It is a feeble acid, and imparts a faint red color to blue litmus. Carbon dioxide decomposes its alkali salts. Like the haloid acids, it reacts with metallic oxides, producing metallic cyanides. From solutions of silver nitrate it precipitates silver cyanide, a white, curdy precipitate.

Transpositions.—(1) The aqueous acid decomposes readily upon standing, yielding ammonium formate and brown substances. The presence of a very slight quantity of stronger acid renders it more stable. When warmed with alkalies or mineral acids it breaks up into formic acid and ammonia:

$$CNH + 2H_2O = CHO.OH + NH_3.$$

(2) Dry prussic acid combines directly with the gaseous halogen hydrides (p. 232) to form crystalline compounds. With hydrochloric acid it probably yields *Formimide chloride*, $(H.CCl = NH)_2HCl$ (B. **16**, 352). The acid also unites with some metallic chlorides, *e. g.*, Fe_2Cl_6, $SbCl_5$.

(3) Nascent hydrogen (zinc and hydrochloric acid) reduces it to methylamine (p. 162).

(4) When hydrogen cyanide unites with *aldehydes* and *ketones*, the double union between carbon and oxygen in the latter compounds is severed, and cyanhydrins, the *nitriles* of *a*-oxyacids, are produced. These, by this means, are obtained by a nucleus synthesis. This rather important synthesis has become especially interesting for the upbuilding of the aldoses, to which class of derivatives *grape-sugar* belongs.

(5) Prussic acid, or potassium cyanide, adds itself to many α,β-unsaturated carboxylic acids, producing thereby saturated nitrilo carboxylic acids (A. **293**, 338).

For further addition reactions of prussic acid, compare formimido ether (p. 232) and isouretine (p. 233).

Constitution.—The production of prussic acid from formamide on the one side, and its reconversion into ammonium formate, are proofs positive of its being the nitrile of formic acid (see acid nitriles). Its formation from chloroform and from acetylene argue also for the formula $H.C\equiv N$. The replacement of hydrogen, combined with carbon, by metals is shown also by *acetylene* (p. 97) and other carbon compounds containing negative groups, *e. g.*, the *nitro-ethanes* (p. 154). However, on replacing the metal atoms in the salts by alkyls, two classes of derivatives are obtained. The one series has the alkyls united to carbon, as required by the formula $H.C\equiv N$: *nitriles* of monocarboxylic acids, *e. g.*, $CH_3.CN$. In the other class the alkyls are joined to nitrogen: *isonitriles* or *carbylamines*, *e. g.*, $C = N.CH_3$. The latter are nitrogen-containing derivatives of *carbon monoxide*, and will be discussed after this body. In many respects the deportment of prussic acid recalls that of the isonitriles, hence in recent years the formula $HN = C$ has also been brought forward for it, and many of the reactions of potassium cyanide conform better with the isonitrile formula, $K.N = C$, than with $K.C\equiv N$, the formula usually assigned to this salt (A. **287**, 263). The formation of acetonitrile from prussic acid and diazomethane argues for the nitrile formula of hydrogen cyanide (B. **28**, 857).

Detection.—To detect small quantities of free prussic acid or its soluble salts, saturate the solution under examination with caustic potash, add a solution of a ferrous salt, containing some ferric salt, and boil for a short time. Add hydrochloric acid to dissolve the precipitated iron oxides. If any insoluble Prussian blue should remain, it would indicate the presence of hydrocyanic acid. The following reaction is more sensitive. A few drops of yellow ammonium sulphide are added to the prussic acid solution, and this then evaporated to dryness. Ammonium sulphocyanide will remain, and if added to a ferric salt, will color it a deep red.

Polymerization of Prussic Acid.—When the aqueous acid stands for some time in contact with caustic alkalies, or with alkaline carbonates, or if prussic acid made from the anhydrous acid be mixed with a small piece of potassium cyanide, not only brown substances separate, but also white crystals, soluble in ether, and having the same percentage composition as hydrocyanic acid. Inasmuch as they break down, on boiling, into *glycocoll*, $NH_2 . CH_2 . CO_2H$, carbon dioxide and ammonia, they are assumed to be the *nitrile of amidomalonic acid*, $(CN)_2CHNH_2$ (B. 7, 767). They decompose at 180°, with explosion and partial reformation of prussic acid.

Salts of Hydrocyanic Acid.—*Cyanides and Double Cyanides*—The importance of the cyanides and double cyanides in analytical chemistry explains the reason for the discussion of prussic acid and its salts in inorganic text-books. In organic chemistry the metallic cyanides serve for the introduction of the *cyanogen group* into carbon compounds (compare *acid nitriles*, *a-ketonic acids*, etc.).

The alkali cyanides may be formed by the direct action of these metals upon *cyanogen gas;* thus, potassium burns with a red flame in *cyanogen*, at the same time yielding potassium cyanide, $C_2N_2 + K_2 = 2CNK$. They are also produced when nitrogenous organic substances are heated together with alkali metals. The strongly basic metals dissolve in hydrocyanic acid, forming cyanides. A more common procedure is to act with the acid upon metallic oxides and hydroxides:

$$CNH + KOH = CNK + H_2O; \; 2CNH + HgO = Hg(CN)_2 + H_2O.$$

The insoluble cyanides of the heavy metals are obtained by the double decomposition of the metallic salts with potassium cyanide.

The cyanides of the light metals, especially the alkali and alkaline earths, are easily soluble in water, react alkaline, and are decomposed by acids, even carbon dioxide, with elimination of hydrogen cyanide; yet they are very stable, even at a red heat, and sustain no change. The cyanides of the heavy metals, however, are mostly insoluble, and are only decomposed, or not at all, by the strong acids. When ignited, the cyanides of the noble metals suffer decomposition, breaking up into cyanogen gas and metals.

The following simple cyanides are especially important in organic chemistry:

Potassium Cyanide, CNK.—Consult v. Richter's "Inorganic Chemistry" for method of preparation, properties, and technical applications of this salt.

Its aqueous or alcoholic solution becomes brown in color on exposure to the air; it decomposes rapidly, on boiling, into potassium formate and ammonia. When fused in the air, as well as with easily reducible metallic oxides, the salt absorbs oxygen and is converted into *potassium isocyanate* (see this). When acid haloids or alkyl sulphates are heated with potassium cyanide, acid nitriles with varying amounts of isomeric carbylamines or isonitriles are produced. Many organic halogen substitution products are transposed into nitriles through the agency of potassium cyanide. Ethyl hypochlorite and potassium cyanide yield cyanimidocarbonic ester a reaction which argues for the isonitrile formula of potassium cyanide (A. **287**, 274).

Ammonium Cyanide, NH_4CN, is formed by the direct union of CNH with ammonia, by heating carbon in ammonia gas, by the action of ammonia upon chloroform (p. 228). by the action of the silent electric discharge upon *methane* and nitrogen, and by conducting carbon monoxide and ammonia through red-hot tubes. It is best prepared by subliming a mixture of potassium cyanide or dry ferrocyanide with ammonium chloride. It consists of colorless cubes, easily soluble in alcohol, and subliming at 40°, with partial decomposition into NH_3 and CNH. When preserved it becomes dark in color and decomposes. It yields *methylene amido-acetonitrile* (compare glycocoll).

Mercuric Cyanide, $Hg(CN)_2$, is obtained by dissolving mercuric oxide in hydrocyanic acid, or by boiling Prussian blue (8 parts) and mercuric oxide (1 part) with water until the blue coloration disappears. It dissolves readily in hot water (in 8 parts cold water), and crystallizes in bright, shining, quadratic prisms. When heated it yields cyanogen and mercury. It forms acetyl cyanide with acetyl chloride (see pyroracemic acid).

Silver Cyanide, AgCN, combines with alkyl iodides to yield addition products, which pass into isonitrile when they are heated (p. 236).

The chief use of potassium cyanide is in the preparation of acid nitriles of various kinds. This is done by bringing it into double decompositions with alkylogens, alkyl sulphates, and halogen substitution products of the fatty acids. In many instances *mercury cyanide* or *silver cyanide* is preferable, *e.g.*, in the formation of *a-ketonic nitriles* from acid chlorides or bromides. It is interesting to note that by the interaction of alkyl iodides and silver cyanide *isonitriles* or *carbylamines* are formed; in them the alcohol radical is joined to nitrogen. (See page 237 for the explanation.)

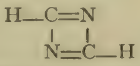
Compound Metallic Cyanides.—The cyanides of the heavy metals insoluble in water dissolve in aqueous potassium cyanide, forming crystallizable double cyanides, which are soluble in water. Most of these compounds behave like double salts. Acids decompose them in the cold, with disengagement of hydrocyanic acid and the precipitation of the insoluble cyanides:

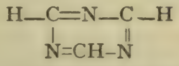
$$AgCN\,.\,KCN + HNO_3 = AgCN + KNO_3 + CNH.$$

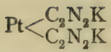
In others, however, the metal is in more intimate union with the cyanogen group, and the metals in these cannot be detected by the usual reagents. Iron, cobalt, platinum, also chromium and manganese in their *ic* state, form cyanogen derivatives of this class. The stronger acids do not eliminate prussic acid from them, even in the cold, but hydrogen acids are set free, and these are capable of producing salts:

$$\underset{\text{Potassium Ferrocyanide}}{Fe(CN)_6K_4} + 4HCl = \underset{\text{Hydroferrocyanic Acid.}}{Fe(CN)_6H_4} + 4KCl.$$

Many chemists refer these complex metallic acids to hypothetical, polymeric prussic acids:

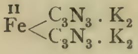

Di-hydrocyanic Acid


Tri-hydrocyanic Acid.



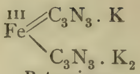
$$\mathrm{Pt}{<}\begin{array}{l}C_2N_2K\\ C_2N_2K\end{array}$$

Potassio-platinum Cyanide



$$\overset{\mathrm{II}}{\mathrm{Fe}}{<}\begin{array}{l}C_3N_3\cdot K_2\\ C_3N_3\cdot K_2\end{array}$$

Potassium Ferrocyanide



$$\overset{\mathrm{III}}{\mathrm{Fe}}\begin{array}{l}\diagup\!\!\diagup C_3N_3\cdot K\\ \diagdown C_3N_3\cdot K_2\end{array}$$

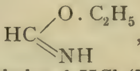
Potassium Ferricyanide.

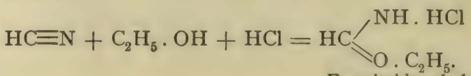
The most important compound metallic cyanides, particularly *potassium ferrocyanide* or *yellow prussiate of potash*, the starting-out substance for the preparation of cyanogen derivatives, have already received attention in inorganic chemistry.

Sodium Nitroprusside, $Fe(CN)_5(NO)Na_2 + 2H_2O$.—Hydro-nitro-prussic acid, whose constitution has not yet been determined (B. **29**, R. 409), is formed when nitric acid acts upon potassium ferrocyanide. The filtrate from the saltpetre, neutralized with sodium carbonate, yields the salt in beautiful red rhombic prisms, readily soluble in water.

It serves as a very delicate reagent for alkaline sulphides and hydrogen sulphide, which give with it an intense violet coloration.

Formimido-ether, *formhydroxamic acid*, *formylchloridoxime*, *formamidine*, *thioformethylimide*, and *formamidoxime* are intimately related to prussic acid and formamide. They are representatives of groups of bodies which appear also with acetic acid and its homologues.

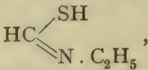
The *formimido-ethers*, such as  $HC{<}\begin{array}{l}O\cdot C_2H_5\\ NH\end{array}$, are only known in their salts. They are obtained from CNH, alcohol and HCl (B. **16**, 354, 1644):

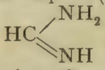


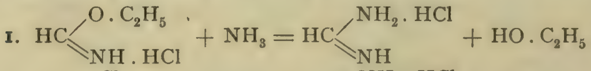
$$HC{\equiv}N + C_2H_5\cdot OH + HCl = HC{<}\begin{array}{l}NH\cdot HCl\\ O\cdot C_2H_5.\end{array}$$

Formimido-ethyl Ether.

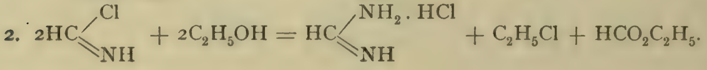
Upon standing with alcohols they pass into esters of orthoformic acid (see this). They yield amidines with ammonia and amines (primary and secondary).

Thioformethylimide,  $HC{<}\begin{array}{l}SH\\ N\cdot C_2H_5\end{array}$, boiling at 125° (14 mm.), is produced by the union of ethyl isocyanide, in alcoholic solution, with hydrogen sulphide. It is a yellow oil, with an odor like that of sulphur (A. **280**, 297).

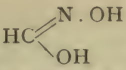
Formamidine, Methenylamidine,  $HC{<}\begin{array}{l}NH_2\\ NH\end{array}$, is only known in its salts. Its chlorhydrate is obtained (1) by the action of ammonia upon *formimido-ethyl-ether chlorhydrate* (B. **16**, 375, 1647); (2) from formimide chloride, the addition product of hydrochloric acid and prussic acid, when it is digested with alcohol:

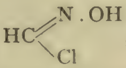


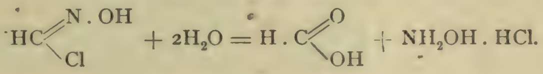
$$1.\ HC{<}\begin{array}{l}O\cdot C_2H_5\\ NH\cdot HCl\end{array} + NH_3 = HC{<}\begin{array}{l}NH_2\cdot HCl\\ NH\end{array} + HO\cdot C_2H_5$$



$$2.\ 2HC{<}\begin{array}{l}Cl\\ NH\end{array} + 2C_2H_5OH = HC{<}\begin{array}{l}NH_2\cdot HCl\\ NH\end{array} + C_2H_5Cl + HCO_2C_2H_5.$$

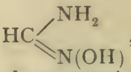
Formhydroxamic Acid,  $\mathrm{HC}\genfrac{}{}{0pt}{}{\diagup \mathrm{N.OH}}{\diagdown \mathrm{OH}}$, is produced when equimolecular quantities of formic ester and hydroxylamine are allowed to stand in a solution of absolute alcohol. It forms brilliant leaflets having a greasy feel. It dissolves readily in water and in alcohol, but sparingly in ether. It melts at 74°. A violent decomposition sets in above this temperature, and then slowly proceeds at the ordinary temperature. The acid yields an intense red coloration with ferric chloride. It reduces Fehling's solution, and its mercury salt in dry condition explodes when it is rubbed (private communication from G. Schröter). Compare B. **25**, 701, for the copper salt.

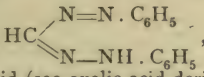
Formylchloridoxime,  $\mathrm{HC}\genfrac{}{}{0pt}{}{\diagup \mathrm{N.OH}}{\diagdown \mathrm{Cl}}$, is a beautifully crystallized, very decomposable compound, with a sharp, penetrating odor. It is produced when fulminates (p. 237) are treated, in the cold, with concentrated sulphuric acid. It dissolves in ether. When its solution is warmed with concentrated hydrochloric acid, it rapidly decomposes into formic acid and hydroxylamine hydrochloride:



$$\mathrm{HC}\genfrac{}{}{0pt}{}{\diagup \mathrm{N.OH}}{\diagdown \mathrm{Cl}} + 2H_2O = \mathrm{H.C}\genfrac{}{}{0pt}{}{\diagup \mathrm{O}}{\diagdown \mathrm{OH}} + NH_2OH.HCl.$$

In aqueous solution the body readily reverts to fulminates. Silver nitrate changes it to silver fulminate and silver chloride. Aniline converts it into phenyl-isouretine (see this), and with ammonia it yields cyanisonitrosoacethydroxamic acid, a derivative of mesoxalic acid (A. **280**, 303).

Formamidoxime, *Methenylamidoxime*, *Isouretine*,  $\mathrm{HC}\genfrac{}{}{0pt}{}{\diagup NH_2}{\diagdown\!\!\diagdown \mathrm{N(OH)}}$, melting at 114°, is isomeric with *urea*, $CO(NH_2)_2$. It forms upon the evaporation of an alcoholic solution of hydroxylamine and hydrogen cyanide (Lossen and Schifferdecker, A. **166**, 295; **280**, 320).

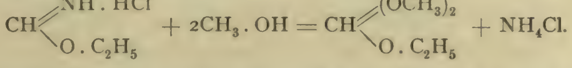
Formazyl Hydride,  $\mathrm{HC}\genfrac{}{}{0pt}{}{\diagup \mathrm{N{=}N}.C_6H_5}{\diagdown\!\!\diagdown \mathrm{N{-}NH}.C_6H_5}$, melting at 119°–120°, is obtained from formazylcarbonic acid (see oxalic acid derivatives).

Derivatives of Orthoformic Acid (p. 224).

Orthoformic Esters are formed (1) when *chloroform* is heated with sodium alcoholates in alcoholic solution (Williamson and Kay, A. **92**, 346):

$$CHCl_3 + 3CH_3.ONa = CH(O.CH_3)_3 + 3NaCl;$$

(2) when formimido-ethers (p. 232) are transposed with alcohols, at which time mixed esters are also produced (Pinner, B. **16**, 1645):



$$\mathrm{CH}\genfrac{}{}{0pt}{}{\diagup \mathrm{NH.HCl}}{\diagdown O.C_2H_5} + 2CH_3.OH = \mathrm{CH}\genfrac{}{}{0pt}{}{\diagup (OCH_3)_2}{\diagdown O.C_2H_5} + NH_4Cl.$$

They are converted by alcoholic alkali into alkali formates, and by glacial acetic acid into acetic esters and ordinary formic esters. Orthoformic ester is changed by ketones and aldehydes into ortho-ethers, *e. g.*, $(CH_3)_2C(O.C_2H_5)_2$ (p. 224), and acetal, $CH_3.CH(O.C_2H_5)_2$ (p. 200). At the same time it passes also into ordinary formic ether (B. **29**, 1007). Orthoformic ester, in the presence of acetic anhydride and aided by heat, combines with acetylacetone, acetoacetic ester and malonic ester to yield ethoxymethenyl derivatives (B. **26**, 2729).

Orthoformic Methyl Ester, $CH(O.CH_3)_3$, boils at 102°. **Orthoformic Ethyl**

Ester, $CH(O.C_2H_5)_3$, boils at 146°. **Orthoformic Allyl Ester,** $CH(OC_3H_5)_3$, boils at 196°–205° (B. **12**, 115).

Chloroform and sodium mercaptides unite to **orthoformic esters** (B. **10**, 185).

Chloroform, Trichlormethane, $CHCl_3$, is obtained: (1) By the chlorination of CH_4 or CH_3Cl; (2) by the action of chloride of lime upon different carbon compounds—*e. g.*, ethyl alcohol, acetone, etc.; (3) by heating *chloral* (p. 197) and other aliphatic bodies having a terminal CCl_3-group—*e. g.*, *trichloracetic acid* and *trichlorphenomalic acid* (see this)—with aqueous potassium or sodium hydroxide:

$$\underset{\text{Chloral}}{CCl_3.CHO} + KOH = CCl_3H + \underset{\substack{\text{Potassium}\\\text{Formate.}}}{CHKO_2}.$$

Chloroform is prepared technically by treating alcohol and acetone with bleaching lime. The latter acts both as an oxidizing and chlorinating substance. The resulting $CCl_3.CHO$ or $CH_3.CO.CCl_3$ is decomposed by slaked lime (Mechanism of the Reaction: Zincke, B. **26**, 501 Anm.). Pure chloroform can be obtained by decomposing pure chloral with caustic potash or, according to R. Pictet, by freezing out crystals of chloroform and then placing this impure substance in a centrifugal machine. Perfectly pure chloroform results in the decomposition of *salicylide-chloroform* (Anschütz, A. **273**, 73).

*Historical.**—Chloroform was discovered in 1831 by Liebig and by Soubeiran. It was not until 1835 that Dumas proved conclusively that it contained hydrogen. In 1847 Simpson, in Edinburgh, introduced chloroform into surgery.

Chloroform is a colorless liquid of an agreeable ethereal odor and sweetish taste. It solidifies in the cold and melts at —62° (B. **26**, 1053). It boils at +61.5°, and its specific gravity at 15° equals 1.5008. It is an excellent solvent for iodine and many other organic substances, some of which crystallize out with "*chloroform of crystallization*," *e. g.*, salicylide (see above). Inhalation of its vapors causes unconsciousness, and at the same time has an anæsthetic effect. It is uninflammable. It forms C_6Cl_6 when it is conducted through tubes heated to redness.

Transformations.—(1) By preservation chloroform is oxidized in sunlight by the oxygen of air to *phosgene* (see this). Chromic acid also converts chloroform into this body. To get rid of the phosgene add about one per cent. of alcohol to the chloroform.

(2) Chlorine changes chloroform to CCl_4.

(3) Potassium formate is produced when chloroform is heated with alcoholic potash:

$$CHCl_3 + 4KOH = CHO.OK + 3KCl + 2H_2O.$$

(4) Ortho-formic acid ester, $CH(O.C_2H_5)_3$, is produced by treating chloroform with sodium alcoholate.

(5) When heated to 180° with alcoholic ammonia, it forms ammonium cyanate and chloride. When caustic potash is present, an energetic reaction takes place at ordinary temperatures. The equation is:

$$CHCl_3 + NH_3 + 4KOH = CNK + 3KCl + 4H_2O.$$

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* Der Schutz des Chloroforms vor Zersetzung am Licht und sein erstes Vierteljahrhundert: E. Biltz, 1892. Der Aether gegen den Schmerz, C. Binz, 1896, S. 54.

(6) *Isonitriles* (p. 236), having extremely disgusting odors, are formed when chloroform is heated with primary bases and caustic potash. This reaction serves both for the detection of chloroform and also of the primary amines.

(7) Chloroform yields an additive product with acetone—*e.g.*, α-oxyisobutyric acid.

(8) It is transposed by sodium acetoacetic ester into m-oxyuvitic acid (see this).

(9) Aromatic oxyaldehydes (see these) are produced when chloroform is digested with phenols and caustic soda.

Bromoform, $CHBr_3$, melts at +7.8°, boils at 151°, has a sp. gr. of 2.9 (at 15°), and is produced by the action of bromine and KOH or lime (Löwig, 1832) upon alcohol or acetone; also from tribrompyroracemic acid.

Iodoform, CHI_3, melting at 120°, was discovered in 1832 by Serullas. Dumas, in 1834, proved that it contained hydrogen, and in 1880 it was applied by Mosetig Moorhof in Vienna as a healing agent. This compound results when iodine and potash act upon ethyl alcohol, or acetone, aldehyde and other substances containing the methyl group. Pure methyl alcohol, however, does not yield iodoform (B. **13**, 1002).

The formation of *tri-iodoaldehyde* and *tri-iodoacetone* precedes the production of the iodoform. These substances naturally would be very unstable. When tri-iodoacetic acid is warmed with acetic acid, or when it is treated with alkali carbonates, it breaks down into iodoform and carbon dioxide.

Iodoform crystallizes in brilliant, yellow leaflets, soluble in alcohol and ether. They are insoluble in water. Its odor is saffron-like. It evaporates at medium temperatures and distils over with aqueous vapor. Digested with alcoholic KOH, HI, or potassium arsenite, it passes into *methylene iodide*, CH_2I_2 (p. 201).

Fluorchloroform, $CHCl_2F$, boils at 14.5°; **Fluorchlorbromoform,** CHClFBr, boils at 38° (B. **26**, R. 781).

Nitroform, *Trinitromethane*, $CH(NO_2)_3$, is an acid. Its ammonium salt is produced when *trinitroacetonitrile* is brought in contact with water, when violent explosions frequently occur. The conditions are unknown (B. 7, 1744):

$$C(NO_2)_3CN \xrightarrow{2H_2O} C(NO_2)_3COONH_4 \xrightarrow[-NH_3]{-CO_2} C(NO_2)_3H.$$

It is a thick, colorless oil, solidifying below 15°, and exploding with violence when rapidly heated.

Formyl-trisulphonic Acid, Methine Trisulphonic Acid, $CH(SO_3H)_3$, is produced by the action of sodium sulphite upon *chloropicrin*, $CCl_3(NO_2)$ (see this), and when fuming sulphuric acid acts upon calcium *methyl-sulphonate* (p. 204). The acid is very stable, even in the presence of boiling alkalies.

In this connection may be mentioned also *dibromnitromethane* (p. 157), *nitromethane disulphonic acid* (A. **161**, 161), and *oxymethane disulphonic acid*, $CH(OH)(SO_3H)_2$ (B. **6**, 1032); *dichlormethane monosulphonic acid*, *dichlormethyl alcohol*, known as acetic esters.

Appendix.—**Carbon Monoxide, Isonitriles** or **Carbylamines,** and **Fulminic Acid.**

Carbon Monoxide, CO, a colorless, combustible gas, the product of the incomplete combustion of carbon, has already been discussed in the inorganic part of this book. The methods for its production and its transformations, which are of importance in organic chemistry, will again be briefly reviewed. Carbon monoxide is obtained (1) from formic acid, (2) from oxalic acid and other acids, like lactic and citric, by the action of sulphuric acid. It is also made (3) from prussic acid, if, in preparing the latter from potassium ferrocyanide, $K_4Fe(CN)_6 . 3H_2O$, concentrated sulphuric acid be substituted for the more dilute acid, and in this manner the prussic acid be changed to formamide, and the latter immediately breaks down into ammonia and carbon monoxide. Formamide yields carbon monoxide upon the application of heat.

Behavior.—(1) Carbon monoxide and hydrogen exposed to the influence of electric discharges yield *methane* (p. 80). Being an unsaturated compound, carbon monoxide unites (2) with oxygen, forming *carbon dioxide;* (3) with sulphur, yielding *carbon oxysulphide;* and (4) with chlorine, to form *carbon oxychloride* or phosgene. It is rather remarkable that it also combines directly with certain metals. (5) With potassium it forms *potassium carbon monoxide* or *potassium hexoxybenzene* (see this), $C_6O_6K_6$; (6) with nickel it yields *nickel carbonyl*, $(CO)_4Ni$ (Mond, Quincke, and Langer, B. **23**, R. 628). It forms alkali formates with the alkaline hydroxides (p. 225), and with (7) sodium methylate and sodium ethylate it yields sodium acetate and propionate.

Carbon Monosulphide, CS, is not yet known (B. **28**, R. 388).

Isonitriles, Isocyanides, or **Carbylamines** are isomeric with the *alkyl cyanides* or the *acid nitriles*, but are distinguished from these in that they have their alkyl group joined to nitrogen. The isonitriles were first prepared in 1866 by Gautier (A. **151**, 239). He employed two methods. The first consisted in allowing alkyl iodides (1 mol.) to act upon silver cyanide (p. 231) (2 mols.), while in the second method the addition products of silver cyanide and the alkyl isonitriles were decomposed by distillation with potassium cyanide:

$$1a. \quad C_2H_5I + 2AgCN = C_2H_5NC . AgCN + AgI$$
$$1b. \quad C_2H_5NC . AgCN + KCN = C_2H_5NC + AgCN . KCN.$$

Shortly after A. W. Hofmann (A. **146**, 107) found that isonitriles were produced by digesting chloroform and primary amines with alcoholic potash:

$$2. \quad C_2H_5NH_2 + HCCl_3 + 3KOH = C_2H_5NC + 3KCl + 3H_2O.$$

3. The isonitriles are produced, too, as by-products, in the preparation of the nitriles from alkyl iodides or sulphates and potassium cyanide (p. 266).

Properties.—The carbylamines are colorless liquids which can be distilled, and possess an exceedingly disgusting odor. They are sparingly soluble in water, but readily soluble in alcohol and ether.

Transpositions.—(1) The isocyanides are characterized by their ready decomposition by dilute acids into *formic acid* and primary amines. This reaction proceeds readily by the action of dilute acids, or by heating with water to 180°

$$C_2H_5 . NC + 2H_2O = C_2H_5 . NH_2 + CH_2O_2.$$

Nitriles, on the other hand, by the absorption of water, pass into the ammonium salts of carboxylic acids:

$$C_2H_5CN + 2H_2O = C_2H_5COONH_4.$$

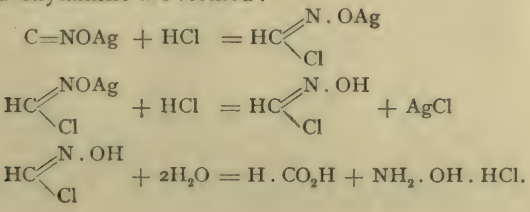
It is, therefore, concluded that in the nitriles the alkyl group is in union with carbon, while in the isonitriles it is linked to nitrogen. Three formulas have been suggested for the isonitriles:

$$\text{I. } C_2H_5\overset{III}{N}{=}\overset{II}{C} \qquad \text{II. } C_2H_5\overset{III}{N}{=}\overset{IV}{C}{=} \qquad \text{III. } C_2H_5\overset{V}{N}{\equiv}\overset{IV}{C}.$$

Nef, who has studied several aromatic isonitriles exhaustively, gives formula **1** the preference (A. **270**, 267). (2) The fatty acids convert isonitriles into alkylized fatty acid amides. (3) The isonitriles, like prussic acid (p. 228), form crystalline derivatives with HCl; probably these are the hydrochlorides of alkyl formimide chlorides, $2CH_3 . NC . 3HCl = [CH_3N = CHCl]_2HCl$, which water decomposes into formic acid and amine bases. (4) Mercuric oxide changes the isonitriles into isocyanic ethers, $C_2H_5N = CO$, with the separation of mercury, just as CO, by absorption of oxygen, becomes CO_2.

Methyl Isocyanide, *Methyl Carbylamine*, *Isoacetonitrile*, CH_3NC, boils at 59°. **Ethyl Isocyanide,** *Ethyl Carbylamine*, C_2H_5NC, boiling at 79°, when heated at from 230° to 250°, rearranges itself to propionitrile. It combines with chlorine to yield ethylisocyan-chloride or ethylimidocarbonyl chloride, a derivative of carbonic acid; with H_2S it forms thioformethylimide (p. 232), and with chloracetyl it produces ethylimidopyruvyl chloride, a derivative of pyroracemic acid (A. **280**, 291).

Fulminic Acid, *Carbyloxime*, C = N . OH, is, according to Nef (A. **280**, 303; B. **27**, 2817), the oxime corresponding to carbon monoxide, and possesses the properties and characteristics of a strong acid. The fulminates have the same percentage composition as the salts of cyanic acid: one of the first examples of isomeric compounds (Liebig, 1823). Free fulminic acid is but slightly known. Its odor is very similar to that of prussic acid, and the acid itself is not any less poisonous than that acid. The acid is formed when the fulminates are decomposed by strong acids. It combines quite readily with the latter,—*e. g.*, it yields formylchloridoxime with hydrochloric acid (p. 233),—but this new body breaks down very easily with the formation of fulminic acid. The deportment of the fulminates toward hydrochloric acid affords some insight into the constitution of fulminic acid itself. First, hydrochloric acid simply adds itself and salts of formylchloridoxime arise, from which, by the absorption of water, formic acid and hydroxylamine are formed:



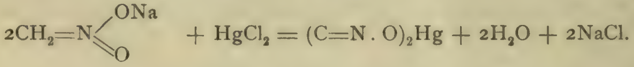
$$C{=}NOAg + HCl = HC\left\langle\begin{matrix}N . OAg\\ Cl\end{matrix}\right.$$

$$HC\left\langle\begin{matrix}NOAg\\ Cl\end{matrix}\right. + HCl = HC\left\langle\begin{matrix}N . OH\\ Cl\end{matrix}\right. + AgCl$$

$$HC\left\langle\begin{matrix}N . OH\\ Cl\end{matrix}\right. + 2H_2O = H . CO_2H + NH_2 . OH . HCl.$$

Mercury fulminate is the most important of the salts. It is applied, technically, as filling material in gun-caps.

Mercury Fulminate, $(C = N . O)_2Hg + \frac{1}{2}H_2O$ (B. **18**, R. 148), is formed (1) by heating a mixture of alcohol, nitric acid, and mercuric nitrate (B. **9**, 787; **19**, 993, 1370); (2) upon adding a solution of sodium nitromethane to a solution of mercuric chloride:



$$2CH_2{=}N\begin{smallmatrix}\diagup ONa \\ \diagdown\!\!\diagdown O\end{smallmatrix} + HgCl_2 = (C{=}N . O)_2Hg + 2H_2O + 2NaCl.$$

There is always produced at the same time a *yellow* basic salt, $\left(Hg{<}{}^{O}_{O}{>}C = NO\right)_2Hg$, which is the sole product in pouring a solution of mercuric chloride into a solution of sodium nitromethane.

Fulminating mercury crystallizes in shining, white needles, which are tolerably soluble in hot water. It explodes violently on percussion and also when acted upon by concentrated sulphuric acid. Concentrated hydrochloric acid evolves CO_2, and yields hydroxylamine hydrochloride and formic acid, a procedure well adapted for the preparation of hydroxylamine (B. **19**, 993). Chlorine gas decomposes mercury fulminate into mercuric chloride, cyanogen chloride, and $CCl_3 . NO_2$. Ammonia converts it into urea and guanidine (see acetyl isocyanate).

Silver fulminate, $C = NOAg$, is prepared after the manner of the mercury salt, and is even more explosive than the latter. Potassium chloride precipitates from hot solutions of silver fulminate one atom of silver as chloride and the double salt, $C_2AgKN_2O_2$, crystallizes from the solution. Nitric acid precipitates from this salt *acid silver fulminate*, $C_2AgHN_2O_2$, a white, insoluble precipitate. On boiling mercury fulminate with water and copper or zinc, metallic mercury is precipitated and copper and zinc fulminates ($C_2CuN_2O_2$ and $C_2ZnN_2O_2$) are produced.

Sodium amalgam changes it to sodium fulminate, $C = NONa$.

In the formation of salts and double salts fulminic acid conducts itself much like hydrocyanic acid. This is readily understood if prussic acid be regarded as hydrogen isocyanide, $C = NH$. Sodium ferrocyanide corresponds to *sodium ferrofulminate*, $(C = NO)_6FeNa_4 + 18H_2O$, which is produced by bringing together a solution of sodium fulminate and ferrous sulphate (A. **280**, 335). It consists of yellow needles.

Dibromnitroacetonitrile or *Dibromglyoxime peroxide*, $\begin{matrix}BrC{=}N{-}O \\ BrC{=}N{-}O\end{matrix}$ or $\begin{matrix}CBr_2NO_2 \\ CN\end{matrix}$ (?), melting at 50°, is produced when bromine acts upon mercury fulminate. This body, when heated with hydrochloric acid, passes into BrH, NH_3, NH_2OH and *oxalic acid*. Aniline probably converts the dibromide into the dioxime of the oxanilide,

$$\begin{matrix}C_6H_5NHC{=}NOH \\ C_6H_5NHC{=}NOH\end{matrix}.$$

Fulminuric Acid, *Nitrocyanacetamide*, $C_3N_3O_3H_3 = CN . CH(NO_2)C\begin{smallmatrix}\diagup OH \\ \diagdown\!\!\diagdown NH\end{smallmatrix}$, is a derivative of tartronic acid. Its alkali salts are obtained by boiling mercuric fulminate with potassium chloride or ammonium chloride and water. The sodium salt is converted by a mixture of sulphuric and nitric acids, into trinitroacetonitrile. To obtain the free acid, decompose the lead salt with hydrogen sulphide. It deflagrates at 145°. Especially characteristic is the *Cuprammonium salt*, $C_3N_3O_3H_3(CuNH_3)$. It consists of glistening dark-blue prisms. (Compare Cyanuric acid.)

Ethyl iodide converts the silver salt at 80°–90° into the **Ethyl Ester**, $C_3H_2N_3O_2(OC_2H_5)$, melting at 133°, which is changed into **Desoxyfulminuric Acid**, Cyanisonitroso-acetamide, a mesoxalic acid derivative, $C_3N_3H_3O_2 = CN . C = N(OH) . C(OH) = NH$, melting at 184° (A. **280**, 331), when boiled with water and alcohol.

ACETIC ACID AND ITS HOMOLOGUES, THE FATTY ACIDS, $C_nH_{2n+1} . CO_2H$.

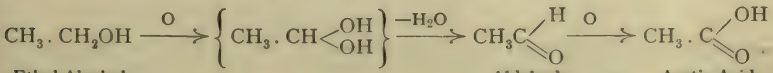
We can regard and also designate all the homologues of acetic acid as mono-, di-, and tri-alkylized acetic acids. Names are then obtained which as clearly express the constitution of the acids as the *carbinol* names show the constitution of the alcohols (p. 110).

The acids of this series are known as *fatty acids*, because their higher members occur in the natural fats. The latter are ester-like compounds of the fatty acids, and are chiefly esters of the trihydric glycerol. On boiling them with caustic potash or soda, alkali salts (soaps) of the fatty acids are formed, and from these the mineral acids release the fatty acids. Hence, the process of converting a compound ester into an acid and an alcohol has been termed *saponification*, and this term has been applied to the conversion of other derivatives of the acids into the acids themselves—*e.g.*, the conversion of nitriles into the corresponding acids.

The lower acids (with exception of the first members) are oils; the higher, commencing with *capric acid*, are solids at ordinary temperatures. The first can be distilled without decomposition; the latter are partially decomposed, and can only be distilled without alteration in vacuo. All of them are readily volatilized with steam. Acids of like structure show an increase in their boiling temperatures of about 19° for every $+ CH_2$. It may be remarked, in reference to the melting points, that these are higher in acids of normal structure, containing an even number of carbon atoms, than in the case of those having an odd number of carbon atoms (see above). The dibasic acids exhibit the same characteristic. As the oxygen content diminishes, the specific gravities of the acids grow successively less, and the acids themselves at the same time approach the hydrocarbons. The lower members are readily soluble in water. The solubility in the latter regularly diminishes with increasing molecular weight. All are easily soluble in alcohol, and especially so in ether. Their solutions redden blue litmus. Their acidity diminishes with increasing molecular weight; this is very forcibly expressed by the diminution of the heat of neutralization and the initial velocity in the etherification of the acids.

The most important, general methods of obtaining the monobasic acids are:

(1) Oxidation of the primary alcohols and aldehydes:



$$CH_3 . CH_2OH \xrightarrow{O} \left\{ CH_3 . CH{<}{}^{OH}_{OH} \right\} \xrightarrow{-H_2O} CH_3C{\lt}{}^{H}_{O} \xrightarrow{O} CH_3 . C{\lt}{}^{OH}_{O}$$

Ethyl Alcohol **Aldehyde** **Acetic Acid.**

In the case of normal primary alcohols with high molecular weight the conversion into the corresponding acids is effected by means of heat:

$$\underset{\text{Cetyl Alcohol}}{C_{15}H_{31}CH_2OH} + NaOH = \underset{\text{Sodium Palmitate.}}{C_{15}H_{31}\,.\,CO_2Na} + 2H_2.$$

(2) By the addition of hydrogen to the unsaturated monocarboxylic acids:

$$\underset{\text{Acrylic Acid}}{CH_2{=}CH\,.\,CO_2H} + 2H = \underset{\text{Propionic Acid.}}{CH_3\,.\,CH_2\,.\,CO_2H.}$$

(3) By the reduction of oxy-acids at elevated temperatures by means of hydriodic acid:

$$CH_3\,.\,CH(OH)CO_2H + 2HI = CH_3\,.\,CH_2\,.\,CO_2H + H_2O + I_2.$$

Or, halogen substituted acids may be reduced by means of sodium amalgam.

Many nucleus-synthetic methods are known for the formation of derivatives of the acids, which can easily be changed to the latter. These methods are important in the building-up of the acids.

(4) *Synthesis of the Acid Nitriles.*—The alkyl cyanides, called also the fatty acid nitriles, are produced by the interaction of potassium cyanide and alkylogens or the alkali salts of the alkyl sulphuric acids. When the alkyl cyanides or fatty acid nitriles are heated with alkalies or dilute mineral acids the cyanogen group is transformed into the carboxyl group, while the nitrogen is changed to ammonia. In this manner formic acid is produced from prussic acid (p. 225):

$$\begin{aligned} CH_3\,.\,CN + 2H_2O + HCl &= CH_3\,.\,CO_2H + NH_4Cl \\ CH_3\,.\,CN + H_2O + KOH &= CH_3\,.\,CO_2K + NH_3. \end{aligned}$$

This method makes the synthesis of acids from alcohols possible.

The change of the nitriles to acids is, in many instances, most advantageously executed by digesting the former with sulphuric acid (diluted with an equal volume of water); the fatty acid will then appear as an oil upon the top of the solution (B. **10**, 262).

To convert the nitriles directly into esters of the acids, dissolve them in alcohol and conduct HCl into this solution, or warm the same with sulphuric acid (B. **9**, 1590).

(5) Action of carbon monoxide upon the sodium alcoholates heated to 160°–200°. This reaction only proceeds smoothly and easily with sodium methylate and ethylate (A. **202**, 294):

$$\underset{\text{Sodium Ethylate}}{C_2H_5\,.\,ONa} + CO = \underset{\text{Sodium Propionate.}}{C_2H_5\,.\,CO_2Na.}$$

Similarly, carbon monoxide and sodium hydroxide yield formic acid (p. 225).

(6) By the action of carbon dioxide upon sodium alkyls (A. **111**, 234). This reaction is only applicable with sodium methide and sodium ethide (p. 184). It may be compared with that in which formic acid is produced by the action of moist carbon dioxide upon potassium (potassium hydride):

$$C_2H_5\,.\,Na + CO_2 = C_2H_5\,.\,CO_2Na.$$

(7) By the action of phosgene gas, $COCl_2$, upon the zinc alkyls. At first acid chlorides are formed, but they subsequently yield acids with water:

$$Zn(CH_3)_2 + 2COCl_2 = 2\underset{\text{Acetyl Chloride}}{CH_3\,.\,COCl} + ZnCl_2, \text{ and}$$

$$CH_3\,.\,CO\,.\,Cl + H_2O = \underset{\text{Acetic Acid.}}{CH_3\,.\,CO\,.\,OH} + HCl.$$

(8) Electrosyntheses of the esters of monocarboxylic acids occur upon electrolyzing mixtures of the salts of fatty acids and the mono-esters of dicarboxylic acids. Butyric

ester, for example, is obtained from potassium acetate and potassium ethyl-succinate (B. **28**, 2427):

$$\begin{array}{l} CH_3|CO_2|K + HOH \\ CH_2|CO_2|K \quad HOH \\ \mid \\ CH_2 . CO_2C_2H_5 \end{array} = \begin{array}{l} \overbrace{CH_3 + CO_2}^{+} \\ \mid \\ CH_2 \qquad CO_2 \\ \mid \\ CH_2\text{–}CO_2 . C_2H_5 \end{array} + \begin{array}{l} \overbrace{KOH \quad\;\; H}^{-} \\ KOH + \;\mid \\ \qquad\quad\;\; H . \end{array}$$

The following methods of formation are based upon the breaking-down of long carbon chains:

(9) The *decomposition of ketones* by oxidation with potassium permanganate and sulphuric acid (p. 211):

$$\underset{\text{Pentadecylmethylketone from Palmitic Acid}}{CH_3[CH_2]_{14} . CO . CH_3} \xrightarrow{O} \underset{\text{Pentadecylic Acid}}{CH_3[CH_2]_{13}CO_2H} + \underset{\text{Acetic Acid.}}{CH_3 . CO_2H}$$

(10) *Decomposition of unsaturated acids* by fusion with caustic potash:

$$\underset{\text{Potassium Angelicate}}{CH_3 . CH : C(CH_3)CO_2K} \xrightarrow{KOH} \underset{\text{Potassium Acetate}}{CH_3 . CO_2K} \text{ and } \underset{\text{Potassium Propionate.}}{CH_3 . CH_2 . CO_2K}$$

(11) *Decomposition of acetoacetic ester*, as well as mono- and dialkylic acetoacetic esters, by concentrated caustic potash:

$$\underset{\text{Acetoacetic Ester}}{CH_3 . CO . CH_2 . CO_2C_2H_5} + 2KOH = CH_3 . CO_2K + CH_3 . CO_2K + C_2H_5OH$$

$$CH_3 . CO.CH(R)CO_2C_2H_5 + 2KOH = CH_3 . CO_2K + CH_2(R)CO_2K + C_2H_5 . OH$$

$$CH_3 . CO . C(R)_2CO_2C_2H_5 + 2KOH = CH_3 . CO_2K + CH(R)_2CO_2K + C_2H_5 . OH.$$

(12) *Decomposition of ketoxime carboxylic acids*, after their rearrangement into acid amides. This reaction is valuable in determining the constitution of the olefine carboxylic acids, from which the ketoxime carboxylic acids can be prepared. (Compare oleic acid, p. 285.)

(13) *Decomposition of dicarboxylic acids*, in which the two carboxyl groups are in union with the same carbon atom. On the application of heat, these sustain a loss of carbon dioxide:

$$\underset{\text{Malonic Acid}}{CH_2{<}\begin{smallmatrix} CO_2H \\ CO_2H \end{smallmatrix}} \longrightarrow CH_3 . CO_2H + CO_2$$

$$CHR{<}\begin{smallmatrix} CO_2H \\ CO_2H \end{smallmatrix} \longrightarrow CH_2RCO_2H + CO_2$$

$$C(R)_2{<}\begin{smallmatrix} CO_2H \\ CO_2H \end{smallmatrix} \longrightarrow CH(R)_2CO_2H + CO_2.$$

The acids produced by the last two methods can be regarded as directly derived from acetic acid, $CH_3 . COOH$, in which 1 and 2H atoms of the CH_3-group are replaced by alkyls; hence the designations *methyl-* and *dimethyl-acetic acid*, etc.:

$\begin{array}{l} CH_2 . CH_3 \\ \mid \\ CO . OH \end{array}$	$\begin{array}{l} CH_2 . C_2H_5 \\ \mid \\ CO . OH \end{array}$	$\begin{array}{l} CH(CH_3)_2 \\ \mid \\ CO . OH \end{array}$
Methyl Acetic Acid or Propionic Acid	Ethyl Acetic Acid or Butyric Acid	Dimethyl Acetic Acid or Isobutyric Acid.

To fully comprehend the importance of the last two methods of formation the following facts may be anticipated:

Acetic ether is the starting-out material for the obtainment of acetoacetic ester, and chloracetic ester for that of malonic ester. *Acetoacetic ester*, $CH_3 . CO . CH_2 . CO . O . C_2H_5$, and *malonic ester*, $CH_2(CO . O . C_2H_5)_2$, contain a CH_2-group, in combination with two CO-groups. One hydrogen atom in a CH_2-group thus situated may be replaced by sodium, and the latter, through the agency of an alkyl iodide, by an alkyl group. In this manner *monoalkylacetoacetic esters*, $CH_3 . CO . CHR . CO . OC_2H_5$, and *monoalkylmalonic esters*, $CHR(COOC_2H_5)_2$, are obtained. And in these monoalkylic derivatives again the second hydrogen atom of the CH_2-group may be substituted by sodium, and this, in turn, through the action of an alkylogen, may be replaced by a similar or a different alcohol radical: the products are then *dialkylacetoacetic esters*, $CH_3 . CO . C(R)_2COOC_2H_5$, and *dialkylmalonic esters*, $C(R)_2(COOC_2H_5)_2$. The ease with which all of the reactions involved in the formation of the alkylmalonic and acetoacetic esters are carried out render these bodies very convenient material for the production of a nucleus synthesis of mono- and dialkylic acetic acids. The breaking-down of malonic acid and the alkylmalonic acids possesses this advantage, that it proceeds in one direction only, whereas the alkylic acetoacetic esters sustain a *ketone decomposition* simultaneously with the *acid decomposition*, with the separation of the carboxyl group (p. 209).

Isomerism.—Every monocarboxylic acid corresponds to a primary alcohol. Hence the number of isomeric monocarboxylic acids of definite carbon content is, as in the instance of the aldehydes, equal to that of the possible primary alcohols (p. 111), possessing a like quantity of carbon. The isomerism is dependent upon the isomerisms of the hydrocarbon radicals in union with the carboxyl group.

There are no possible isomerides of the first three members of the series $C_nH_{2n}O_2$:

HCO_2H	$CH_3 . CO_2H$	$C_2H_5 . CO_2H$
Formic Acid	Acetic Acid	Propionic Acid.

Two structural cases are possible for the fourth member, $C_4H_8O_2$:

$CH_3 . CH_2 . CH_2 . CO_2H$	and	$(CH_3)_2 . CH . CO_2H$
Propyl Carboxylic Acid Butyric Acid		Isopropyl Carboxylic Acid. Isobutyric Acid.

Four isomerides are possible with the fifth member, $C_5H_{10}O_2 = C_4H_9 . CO_2H$, inasmuch as there are four butyl, C_4H_9, groups, etc.

Transformations.—A concise review of their many derivatives was given in the introduction to the monocarboxylic acids. These were obtained in part from the acids, or directly from their salts. Their most important reactions follow:

(1) Acids and alcohols yield *esters* in the presence of hydrochloric or sulphuric acid (p. 253).

(2) Salts and alkylogens, or alkyl sulphates, yield *esters*.

(3) Acids or salts yield, when acted upon by the chlorides of phosphorus, *acid chlorides* (p. 257) and *acid anhydrides* (p. 259).

(4) The ammonium salts of the acids split off water and become *acid amides* (p. 262) and *acid nitriles* (p. 266).

(5) The halogens produce substitution products.

(6) The fatty acids are very stable in the presence of oxidizing agents; they are attacked very slowly. Fatty acids, containing a tertiary group, yield nitroderivatives (B. **15**, 2318) when acted upon by nitric acid.

In discussing the *paraffins*, their *alcohols*, *aldehydes* and *ketones*, methods of producing these bodies were made known, which were based upon the transposition reactions of the fatty acids, their salts or their immediate derivatives. These may be summarized here:

(1) *Paraffins* (p. 84) result in the reduction of higher fatty acids by hydriodic acid.

(2) *Paraffins* (p. 84) are produced when the calcium salts of the fatty acids are distilled with soda-lime.

(3) *Paraffins* (p. 83) result from the electrolysis of concentrated solutions of the potassium salts of the fatty acids.

(4) Acid chlorides and acid anhydrides, when reduced, yield *aldehydes* (p. 113) and *primary alcohols* (p. 189).

(5) Acid chlorides and zinc alkyls yield *ketones* (p. 210) and *tertiary alcohols* (p. 113).

(6) By the interaction of iodine and the silver salts of fatty acids esters of the next lower alcohol are formed (compare p. 252).

(7) When the calcium salts and calcium formate are distilled, *aldehydes* are produced (p. 188).

(8) *Simple* and *mixed ketones* (p. 209) are formed when the calcium salts are distilled alone or in an equimolecular mixture.

(9) The reduction of acid nitriles yields *primary amines;* these, nitrous acid converts into the corresponding alcohols.

(10) Acid amides, when acted upon by bromine and sodium hydroxide, split off CO as carbon dioxide and pass into the next lower series of *primary amines*. This reaction answers for the disintegration of the fatty acids (p. 252).

The constitution of the fatty acids follows from this production from bodies of known constitution and their conversion into the same.

Acetic Acid [*Ethan-acid*], $CH_3.COOH$, Acidum aceticum.—Acetic acid, formed by the spontaneous souring of alcoholic liquids, is the acid which has been longest known. Vinegar and the term "acid" were designated, for example, by the Romans by closely related words. Wood vinegar became known first in the middle ages.

Acetic acid is found in the vegetable kingdom both free and in the form of salts and esters. Thus, it was mentioned under n-hexyl and n-octyl alcohols that they occurred in the form of their *acetic esters* in the ethereal oil of the seed of *Heracleum giganteum* and in the fruit of *Heracleum sphondylium*. The officinal, concentrated acid, as well as the thirty per cent. aqueous solution of the acid, are applied medicinally.

Acetic acid is produced in the decay of many organic substances and in the dry distillation of wood, sugar, tartaric acid, and other compounds; also in the oxidation of numerous carbon derivatives, as it is very stable toward oxidants.

The methods of forming acetic acid, which have any remarkable theoretical value, have already been discussed under the general methods for the production of fatty acids (p. 239); therefore, they will be but briefly noticed here :

(1) The oxidation of ethyl alcohol and acetaldehyde.

(2) The reduction of oxyacetic acid or glycollic acid, $CH_2(OH) . CO_2H$, and the reduction of chlorinated acetic acids—*e. g.*, trichloracetic acid, $CCl_3 . CO_2H$.

Synthetically: (3) From methyl cyanide or acetonitrile.

(4) From sodium methylate and carbon monoxide.

(5) From sodium methide and carbon dioxide.

(6) From phosgene and zinc methide.

By decomposition: (7) By the oxidation of acetone and many mixed methyl ketones.

(8) By the decomposition of many unsaturated acids of the oleic series when fused with caustic potash.

(9) From aceto-acetic ester by means of alcoholic potash.

(10) By heating malonic acid.

Finally, a rather remarkable synthesis of acetic acid consists in letting air and caustic potash act upon acetylene in diffused daylight (Berthelot, 1870):

$$CH\equiv CH + H_2O + O = CH_3 . COOH.$$

Historical.—At the close of the eighteenth century Lavoisier recognized the fact that air was necessary for the conversion of alcohol into acetic acid. Its volume was correspondingly diminished. In 1830 Dumas converted the acid, by means of chlorine, into trichloracetic acid, while the reconversion of the latter into the parent acid, by sodium amalgam and water, was demonstrated by Melsens in 1842. But when, in 1843, Kolbe succeeded in producing *trichloracetic acid* (p. 274) from its elements, the first synthesis of acetic acid was accomplished.

Acetic acid is produced (1) by the oxidation of ethyl alcohol and liquids containing this alcohol. It is customary, depending upon their origin, to distinguish *wine vinegar*, *fruit vinegar*, and *beer vinegar*.

(1) **The Quick-vinegar Process** (Schützenbach, 1823).—The acetic fermentation of alcoholic liquids consists in the transference of the oxygen of the air to the alcohol (Pasteur). This is effected by the acetic ferment, the "mother of vinegar,"—*Mycoderma aceti*, *Micrococcus aceti*, or *Bacterium aceti*,*—the germs of which are always present in the air. In this process, by an enlargement of the contact surface of the alcoholic liquid with the air, there ensues an accelerated oxidation. Large, wooden tubs are filled with shavings previously moistened with vinegar, then the diluted (ten per cent.) alcoholic solutions are poured upon these. The lower part of the tub, exposed in a warm room (25°–30°), is provided with a sieve-like bottom, and all about it are holes permitting the entrance of air to the interior. The liquid

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* Vorlesungen über Bacterien von A. de Bary, 1887. Die Gährungschemie von Adolf Mayer, 1895.

collecting on the bottom is run through the same process two or three times, to insure the conversion of all the alcohol into acetic acid.

(2) *Wood Vinegar Process.*—Considerable quantities of acetic acid are also obtained by the dry distillation of wood in cast-iron retorts. The aqueous distillate, consisting of acetic acid, wood spirit, acetone, and empyreumatic oils, is neutralized with soda, evaporated to dryness, and the residual sodium salt heated to 230°–250°. In this manner, the greater portion of the various organic admixtures is destroyed, sodium acetate remaining unaltered. The salt purified in this way is distilled with sulphuric acid, when acetic acid is set free and purified by further distillation over potassium chromate.

Properties.—Anhydrous acetic acid at low temperatures consists of a leafy, crystalline mass—*glacial acetic acid*—fusing at 16.7°, and forming at the same time a penetrating, acid smelling liquid, of specific gravity 1.0497 at 20°. It boils at 118°, and mixes with water in all proportions. In this case a contraction first ensues, consequently the specific gravity increases until the composition of the solution corresponds to the hydrate, $C_2H_4O_2 + H_2O$ ($= CH_3 . C(OH)_3$); the specific gravity then equals 1.0754 (77–80 per cent.) at 15°. On further dilution, the specific gravity becomes less, until a 50 per cent. solution possesses about the same specific gravity as anhydrous acetic acid. Ordinary vinegar contains about 5–15 per cent. of acetic acid. Acetic acid is an excellent solvent for many carbon compounds. Even the haloid acids dissolve readily in glacial acetic acid (B. **11**, 1221). Pure acetic acid should not decolorize a drop of potassium permanganate. It may be detected by conversion into volatile acetic ether when heated with alcohol and sulphuric acid (p. 255), or by the formation of cacodyl oxide (p. 176).

Acetates.—The acid combines with one equivalent of the bases, forming readily soluble, crystalline salts. It also forms basic salts with iron, aluminium, lead and copper; these are sparingly soluble in water. The alkali salts have the additional property of combining with a molecule of acetic acid, yielding *acid* salts, $C_2H_3KO_2 + C_2H_4O_2$.

Potassium Acetate, $C_2H_3KO_2$, deliquesces in the air and dissolves readily in alcohol. The *acid* salt, $C_2H_3KO_2 . C_2H_4O_2$, crystallizes out in pearly leaflets. It fuses at 148°. The *salt*, $C_2H_3O_2K + 2C_2H_4O_2$, melting at 112°, is decomposed at 170° into acetic acid and the neutral salt.

Sodium Acetate, $C_2H_3NaO_2 + 3H_2O$, crystallizes in large, rhombic prisms. The crystals effloresce on exposure. When heated, the anhydrous salt remains unchanged at 310°.

Ammonium Acetate, $C_2H_3(NH_4)O_2$, is a crystalline mass. Heat applied to the dry salt converts it into water and acetamide. *Calcium Acetate*, $(C_2H_3O_2)_2Ca + H_2O$, and *Barium Acetate*, $(C_2H_3O_2)_2Ba + H_2O$, dissolve readily in water.

Ferrous Acetate, $(C_2H_3O_2)_2Fe$, oxidizes in the air to insoluble basic ferric acetate. *Neutral ferric acetate*, $(C_2H_3O_2)_6Fe_2$, is not crystallizable. On boiling, ferric oxide is precipitated in the form of basic acetate. The same may be said in regard to aluminium acetate. Both salts are applied as mordants in dyeing, as they are capable of uniting with the cotton fiber. The basic salts produced on the application of heat are capable of retaining *dyes*.

Neutral Lead Acetate, $(C_2H_3O_2)_2Pb + 3H_2O$, is obtained by dissolving litharge in acetic acid. The salt forms brilliant four-sided prisms, which effloresce on exposure. It possesses a sweet taste (hence called *sugar of lead*), and is poisonous. If an aqueous solution of sugar of lead be boiled with litharge, *basic lead salts*, of varying lead content, *e. g.*, $C_2H_3O_2PbOH$ and $C_2H_3O_2Pb.O.Pb.O.Pb.C_2H_3O_2$, are produced. Their alkaline solutions find application under the designation—*lead vinegar*. Solutions of basic lead acetates absorb carbon dioxide from the air and deposit *basic carbonates* of lead—white lead.

Lead Tetra-acetate, $(C_2H_3O_2)_4Pb$ is obtained when minium is dissolved in hot glacial acetic acid. From the filtrate colorless monoclinic prisms separate; these melt at 175° (B. **29**, R. 342).

Neutral Copper Acetate, $(C_2H_3O_2)_2Cu + H_2O$, is easily soluble in water. *Basic copper* salts occur in trade under the title of *verdigris*. They are obtained by dissolving copper strips in acetic acid in presence of air. The double salt of acetate and arsenite of copper is the so-called *Schweinfurt Green—mitis green*.

Silver Acetate, $C_2H_3O_2Ag$, separates in brilliant needles or leaflets. The salt is soluble in 98 parts water at 14° C.

The *decompositions of the acetates* have been previously given at various points; summarized they are:

(1) Potassium acetate, when electrolyzed, yields *ethane* or *dimethyl* (p. 76).

(2) Sodium acetate, heated with soda lime, yields *methane* (p. 81).

(3) Potassium acetate and arsenious oxide, on the application of heat, yield *cacodylic oxide* (p. 177).

(4) Ammonium acetate loses water on the application of heat with the formation of *acetamide* (p. 265).

(5) Calcium acetate is decomposed by heat into *acetone* (p. 214).

(6) Calcium acetate and calcium formate, heated together, yield *aldehyde* (p. 195).

(7) Calcium acetate and the calcium salts of higher fatty acids yield mixed methyl alkyl-ketones when they are heated (p. 210).

PROPIONIC ACID. BUTYRIC ACIDS. VALERIC ACIDS.

The following table contains the melting points (B. **29**, R. 344), the boiling points, and the specific gravities of the normal acids and their isomerides:

Name.	Formula.	M. P.	B. P.	Specific Gravity.
Propionic Acid, Methyl Acetic Acid, ...	$CH_3.CH_2—CO_2H$	—36.5°	140°	0.9920 (18°)
n-Butyric Acid, Ethyl Acetic Acid, ...	$CH_3.(CH_2)_2CO_2H$	—	163°	0.9587 (20°)
Isobutyric Acid, Dimethyl Acetic Acid, ...	$\genfrac{}{}{0pt}{}{CH_3}{CH_3}>CH—CO_2H$	—79°	155°	0.9490 (20°)
n-Valeric Acid, n-Propyl Acetic Acid, ...	$CH_3(CH_2)_3CO_2H$	—59°	186°	0.9568 (0°)
Isovaleric Acid, Isopropyl Acetic Acid, ...	$C_3H_7.CH_2—CO_2H$	—51°	174°	0.9470 (0°)
Methyl-ethyl Acetic Acid, . .	$\genfrac{}{}{0pt}{}{CH_3}{C_2H_5}>CH—CO_2H$	—	175°	0.9410 (21°)
Trimethyl Acetic Acid, Pivalic Acid, ...	$(CH_3)_3C.CO_2H$	+35°	163°	—

Propionic Acid, Methylacetic Acid [Propan-acid], $CH_3 . CH_2 . CO_2H$, may be prepared by the methods in general use in making fatty acids; (1) by the oxidation of normal propyl alcohol and propylaldehyde with chromic acid; (2) by reduction of *acrylic acid* (p. 280) and *propargylic acid* (p. 287); (3) by reduction of *lactic acid*, $CH_3 . CH(OH) . CO_2H$, and glyceric acid; (4) (synthetically) from *ethyl alcohol* through its conversion, by means of ethyl iodide, into ethyl cyanide or propionitrile; (5) from sodium ethylate and carbon monoxide; (6) from sodium ethide and carbon dioxide; (7) (*by decomposition*) in the oxidation of methyl-ethyl, methyl-propyl and diethyl-ketone; (8) by the action of alcoholic potash upon methyl aceto-acetic ester with the simultaneous production of ethyl methyl ketone; (9) from methylmalonic acid or isosuccinic acid by the application of heat.

Its formation from malate and lactate of calcium by fermentation is worthy of note (B. **12**, 479; **17**, 1190). Gottlieb first discovered propionic acid in 1847, when he fused cane sugar with caustic potash. Dumas gave the acid its name, derived from πρῶτος, *the first*, πίων, *fat*, because when treated in aqueous solution with calcium chloride it separated as an oil. It is the first acid which in its behavior approaches the higher fatty acids.

The *barium salt*, $(C_3H_5O_2)_2Ba + H_2O$, crystallizes in rhombic prisms. The *silver salt*, $C_3H_5O_2Ag$, dissolves sparingly in water.

Butyric Acids, $C_4H_8O_2$.

Two isomeric acids are possible:

(1) **Normal Butyric Acid**, *Ethyl Acetic Acid* [*Butan acid*], butyric acid of fermentation, occurs free and also as the glycerol ester in the vegetable and animal kingdoms, especially in the butter of cows (to the amount of five per cent., together with considerable of the glycerides of palmitic, stearic, and oleic acids), in which Chevreul found it, in the course of his classic investigations upon the fats. It exists as hexyl ester in the oil of *Heracleum giganteum*, and as octyl ester in *Pastinaca sativa*. It has been observed free in the perspiration and in the fluids of the flesh. It may be obtained by the usual methods employed for the preparation of fatty acids, and is produced in the butyric fermentation of sugar, starch and lactic acid, and in the decay and oxidation of albuminoid bodies.

Ordinarily the acid is obtained by the fermentation of sugar or starch, induced by the previous addition of decaying substances, *e. g.*, cheese, in the presence of calcium or zinc carbonate, intended to neutralize the acids, which are formed. According to Fitz, the butyric fermentation of glycerol or starch is most advantageously evoked by the direct addition of schizomycetes, especially *Bacillus subtilis* and *Bacillus boocopricus* (B. **11**, 49, 53; **29**, 2726).

Butyric acid is a thick, rancid-smelling liquid, which solidifies when cooled. It boils at 163°. It dissolves readily in water and alcohol, and may be thrown out of solution by salts. The *ethyl ester* boils at 120°.

The *calcium salt*, $(C_4H_7O_2)_2Ca + H_2O$ (A. **213**, 67), yields brilliant leaflets, and is less soluble in hot than in cold water (in 3.5 parts at 15°); therefore the latter grows turbid on warming.

(2) **Isobutyric Acid**, $(CH_3)_2 . CH . CO_2H$, dimethyl-acetic acid [Methyl Propan-acid], is found free in carobs (*Ceratonia siliqua*),

as octyl ester in the oil of *Pastinaca sativa*, and as ethyl ester in croton oil. It is prepared according to the general methods (p. 239), while concentrated nitric acid converts it into *dinitropropane* (p. 158). Potassium permanganate oxidizes it to α-oxyisobutyric acid.

Isobutyric acid bears great similarity to normal butyric acid, but is not miscible with water.

The *calcium salt*, $(C_4H_7O_2)_2Ca + 5H_2O$, dissolves more readily in hot than in cold water.

Valeric Acids, $C_5H_{10}O_2$. There are four possible isomerides (compare table, p. 246):

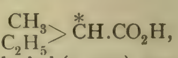
(1) **Normal Valeric Acid,** n-*Propylacetic Acid* [Pentan-acid], $CH_3 . (CH_2)_3 . CO_2H$, is formed according to the usual methods (p. 239).

Ordinary valeric acid, or baldrianic acid, occurs free, and as esters in the animal and vegetable kingdoms, chiefly in the small valerian root (*Valeriana officinalis*), and in the root of *Angelica Archangelica*, from which it may be isolated by boiling with water or a soda solution. It is a mixture of isovaleric acid with the optically active methyl-ethyl acetic acid, and is therefore also active. A similar artificial mixture may be obtained by oxidizing the amyl alcohol of fermentation (p. 127) with a chromic acid solution. Valeric acid combines with water and yields an officinal hydrate, $C_5H_{10}O_2 + H_2O$, soluble in 26.5 parts of water at 15°.

(2) **Isovaleric Acid,** *Isopropyl Acetic Acid* [3 Methylbutan-acid], $(CH_3)_2 . CH . CH_2 . CO_2H$, may be synthetically obtained by some of the methods described on p. **240**. It is an oily liquid with an odor resembling that of old cheese.

Potassium permanganate oxidizes isovaleric acid to β-oxyisovaleric acid, $(CH_3)_2 . C(OH) . CH_2 . CO_2H$. Concentrated nitric acid attacks, in addition, the CH-group, forming methyloxysuccinic acid, *β-nitroisovaleric acid*, $(CH_3)_2 . C(NO_2) . CH_2 . CO_2H$, and *β-dinitropropane*, $(CH_3)_2C(NO_2)_2$ (B. **15**, 2324).

The isovalerates generally have a greasy touch. When thrown in small pieces upon water they have a rotary motion, dissolving at the same time. *Barium salt*, $(C_5H_9O_2)_2Ba$. The *calcium salt*, $(C_5H_9O_2)_2Ca + 3H_2O$, stable, readily soluble needles. The *zinc salt*, $(C_5H_9O_2)_2Zn + 2H_2O$, crystallizes in large, brilliant leaflets; when the solution is boiled a basic salt separates.

(3) **Methyl-ethyl Acetic Acid,** [2-Methyl-butan-acid],  $\genfrac{}{}{0pt}{}{CH_3}{C_2H_5}{>}\overset{*}{C}H.CO_2H$, contains an asymmetric carbon atom, and, like its corresponding alcohol (p. 127), may exist in two optically active and one optically inactive modification. The optically inactive form has been synthesized, and has also been resolved by means of its brucine salts into its optically active components. The l-salt dissolves with difficulty. The specific rotatory power of the optically active methyl-ethyl acetic acids is:

$$[\alpha]_D = \pm 17.85° \text{ (B. } \mathbf{29}\text{, 52).}$$

Calcium salt, $(C_5H_9O_2)_2Ca + 5H_2O$.

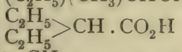
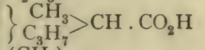
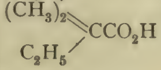
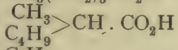
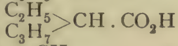
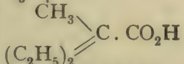
An optically active *methyl-ethyl acetic* acid is present in the naturally occurring valeric acid, together with isopropyl-acetic acid, but in consequence of the slight crystallizing power of its salts it has not been isolated from the isopropyl-acetic acid (A. **204**, 159), and is obtained by the oxidation of the amyl alcohol of fermentation (see above).

(4) **Trimethyl Acetic Acid**, $(CH_3)_3C . CO_2H$ (*Pivalic acid*), [Dimethylpropanacid], is formed from tertiary butyl iodide, $(CH_3)_3CI$ (p. 140), by means of the cyanide, also by the oxidation of pinacoline (p. 216). The acid is soluble in 40 parts H_2O at 20°, and has an odor resembling that of acetic acid.

Barium salt, $(C_5H_9O_2)_2Ba + 5H_2O$. *Calcium salt*, $(C_5H_9O_2)_2Ca + 5H_2O$.

HIGHER FATTY ACIDS.

The subjoined table contains the melting and boiling points of the higher fatty acids, beginning with those containing six carbon atoms. The boiling points enclosed in parentheses were determined under 100 mm. pressure:

Name.	Formula.	M. P.	B. P.
n-Hexoic Acid, n-Caproic Acid,	$CH_3 . (CH_2)_4CO_2H$	+ 8°	205°
Isobutyl Acetic Acid (B. 27, R. 191),	$(CH_3)_2CH[CH_2]_2CO_2H$	—	198°
Sec. Butyl Acetic Acid (B. 26, R. 931),	$(C_2H_5)(CH_3)CHCH_2 . CO_2H$	—	174°
Diethylacetic Acid,	 $\begin{matrix}C_2H_5\\C_2H_5\end{matrix}{>}CH . CO_2H$	—	190°
Methyl-n-propyl Acetic Acid, Methyl-isopropyl Acetic Acid,	 $\begin{matrix}CH_3\\C_3H_7\end{matrix}{>}CH . CO_2H$	—	191°
Dimethyl-ethyl Acetic Acid,	 $\begin{matrix}(CH_3)_2\\C_2H_5\end{matrix}{>}CCO_2H$	−14°	187°
n-Heptoic Acid, Oenanthylic Acid,	$CH_3(CH_2)_5CO_2H$	−10.5°	223°
Methyl-n-butyl Acetic Acid,	 $\begin{matrix}CH_3\\C_4H_9\end{matrix}{>}CH . CO_2H$	—	210°
Ethyl-n-propyl Acetic Acid,	 $\begin{matrix}C_2H_5\\C_3H_7\end{matrix}{>}CH . CO_2H$	—	209°
Methyl-diethyl Acetic Acid,	 $\begin{matrix}CH_3\\(C_2H_5)_2\end{matrix}{>}C . CO_2H$	—	208°
n-Octoic Acid, Caprylic Acid,	$CH_3(CH_2)_6CO_2H$	16.5°	237°
n-Nonoic Acid, Pelargonic Acid,	$CH_3(CH_2)_7CO_2H$	12.5°	254°
n-Capric Acid,	$CH_3(CH_2)_8CO_2H$	31.4°	270°
n-Undecylic Acid,	$CH_3(CH_2)_9CO_2H$	28.5°	(212.5°)
n-Lauric Acid,	$CH_3(CH_2)_{10}CO_2H$	43.5°	(225°)
n-Tridecylic Acid,	$CH_3(CH_2)_{11}CO_2H$	40.5°	(236°)
n-Myristic Acid,	$CH_3(CH_2)_{12}CO_2H$	53.8°	(220.5°)
n-Pentadecatoic Acid (B. 27, R. 191),	$CH_3(CH_2)_{13}CO_2H$	51°	(260°)
n-**Palmitic Acid**,	$CH_3(CH_2)_{14}CO_2H$	62°	(278.5°)
n-Margaric Acid,	$CH_3(CH_2)_{15}CO_2H$	59.9°	(280.5°)
n-**Stearic Acid**,	$CH_3(CH_2)_{16}CO_2H$	69.2°	(291°)
Di-n-octyl Acetic Acid,	$[CH_3(CH_2)_7]_2CHCO_2H$	38.5°	—
n-Arachidic Acid,	$C_{20}H_{40}O_2$	75°	—
Behenic Acid,	$C_{22}H_{44}O_2$	83°	—
Cerotic Acid,	$C_{25}H_{50}O_2$	78°	—
Melissic Acid,	$C_{30}H_{60}O_2$	90°	—

The normal fatty acids in the preceding list, having an even number of carbon atoms, occur almost exclusively in the natural oils and fats, which are chiefly glycerides of these acids. Palmitic and stearic acids possess great technical importance.

Caproic Acid, n-*Hexylic Acid*, $CH_3(CH_2)_4CO_2H$, occurs in the form of its glycerol ester in cow's butter, goat butter, and in cocoanut oil. It is produced, together with butyric acid, in the butyric fermentation.

Oenanthylic Acid, n-*Heptylic Acid*, $CH_3(CH_2)_5CO_2H$, can easily be obtained as an oxidation product of *oenanthol* (p. 196).

Caprylic Acid, n-*Octoic Acid*, $CH_3(CH_2)_6CO_2H$, occurs as glycerol ester in goat butter and in many fats and oils; also in the fusel-oil of wine.

Pelargonic Acid, n-*nonoic acid*, $CH_3(CH_2)_7CO_2H$, is present in the leaves of *Pelargonium roseum*, and is prepared by the oxidation of oleic acid and oil of rue (methyl-n-nonyl ketone, p. 216). It may also be obtained by the fusion of undecylenic acid with potassium hydroxide.

Capric Acid, n-*Decylic Acid*, $CH_3(CH_2)_8CO_2H$, is present in butter, goat butter, in cocoanut oil and in many fats, and as amyl ester in fusel oil. It is the first normal acid that is solid at the ordinary temperature.

n-**Undecylic Acid**, $CH_3(CH_2)_9CO_2H$, is obtained by reduction of undecylenic acid from castor oil.

Lauric Acid, n-*Dodecylic Acid*, $CH_3(CH_2)_{10}CO_2H$, occurs as glycerol-ester in the fruit of *Laurus nobilis*, and in pichurium beans. It is found as *cetyl ester* in spermaceti.

Myristic Acid, n-*Tetradecylic Acid*, $CH_3 . (CH_2)_{12}CO_2H$, occurs in muscat butter (from *Myristica moschata*), in spermaceti and oil of cocoanut, in *myristin* (B. **18**, 2011; **19**, 1433), in earth-nuts (B. **22**, 1743), in ox-bile (B. **25**, 1829), and as free acid, as well as methyl ester, in iris root (B. **26**, 2677).

Palmitic Acid, n-*Hexadecylic Acid*, $CH_3(CH_2)_{14}CO_2H$.—The glycerol ester of this acid and that of stearic acid and oleic acid constitute the principal ingredients of solid animal fats. Palmitic acid occurs in rather large quantities, partly uncombined, in palm oil. Spermaceti is the *cetyl-ester* of the acid, while the *myricyl ester* is the chief constituent of beeswax. The acid is most advantageously obtained from olive oil, which consists almost exclusively of the glycerides of palmitic and oleic acids (see latter); also, from Japanese beeswax, a glyceride of palmitic acid (B. **21**, 2265). The acid is artificially made by heating cetyl alcohol with soda lime to 270°; also by fusing together *oleic acid* and potassium hydroxide.

Margaric Acid, $C_{17}H_{34}O_2$, does not apparently exist naturally in the fats. It is made in an artificial way by boiling cetyl cyanide with caustic potash.

Stearic Acid, n-*Octodecylic Acid*, $CH_3(CH_2)_{16}CO_2H$, is associated with palmitic and oleic acids as a mixed glyceride in solid animal fats—the tallows. Its name is derived from *στέαρ* = tallow.

Arachidic Acid, $CH_3(CH_2)_{18}CO_2H$, occurs in earth-nut oil (from *Arachis hypogæa*). It has been obtained synthetically from aceto-acetic ester and octodecyl iodide (from stearyl aldehyde) (B. **17**, R. 570). For products derived from arachidic acid, see B. **29**, R. 852. *Theobromic Acid*, derived from cacao butter, melts at 72°, and appears to be identical with arachidic acid.

Behenic Acid, $C_{22}H_{44}O_2$, is found in the oil obtained from *Moringa oleïfera*, and has been prepared by the reduction of iodobehenic acid from erucic acid (B. **27**, R. 577).

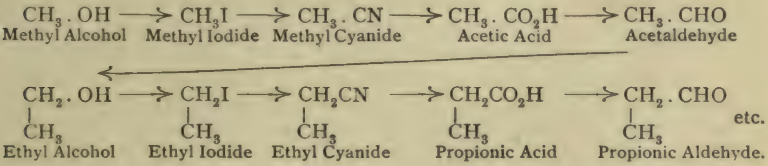
Cerotic Acid, $C_{25}H_{50}O_2$ (B. **29**, R. 995), occurs. together with melissic acid, in a free condition in beeswax, and may be extracted from this on boiling with alcohol. As ceryl ester, it constitutes the chief ingredient of *Chinese wax*. Its name is derived from *cera* = wax.

Melissic Acid, $C_{30}H_{60}O_2$, is formed from myricyl alcohol (p. 130) when the latter is heated with soda-lime. It is a waxy substance, melting at 88°, and is really, as it appears, a mixture of two acids.

The acids mentioned in the table, but not described here, have been prepared by the usual synthetic methods. Some of them will be encountered later in the form of oxidation or reduction products of complicated, complex aliphatic derivatives.

SYNTHESIS AND DECOMPOSITION OF THE FATTY ACIDS.

The synthetic methods presented for the production of the fatty acids are not equally well adapted for this purpose. Thus, methods 5, 6, and 7 (p. 240) are restricted to the synthesis of the simplest members of the series. Reactions more satisfactory than these, and especially fit for the synthesis of the higher monodialkylic acetic acids, are based on the deportment of acetoacetic ester and malonic ester (methods 10 and 11). However, from the very nature of affairs, trialkylic acetic acids can not be synthesized in this way. It is only the fourth method of formation—the synthesis of an acid cyanide from the iodide of an alcohol containing an atom less of carbon than the cyanide and the acid derived from it—that will lead to the synthesis of not only mono- and di-, but also of trialkylic acetic acids. The nitriles of the latter—*e.g.*, of *trimethyl acetic acid*, *dimethylethyl acetic acid*, and *diethylmethyl acetic acid*—have been obtained from the iodides of the corresponding tertiary alcohols. The nitrile synthesis renders the formation of acids from alcohols possible, and inasmuch as acids can be reduced to aldehydes and alcohols by the fourth transposition method (p. 243), the synthesis of these two classes of bodies is made possible. Lieben, Rossi, and Janecek (A. **187**, 126), beginning with methyl alcohol, systematically prepared the normal acids and corresponding alcohols up to *oenanthic acid*, according to the following scheme:



$$\underset{\text{Methyl Alcohol}}{CH_3.OH} \longrightarrow \underset{\text{Methyl Iodide}}{CH_3I} \longrightarrow \underset{\text{Methyl Cyanide}}{CH_3.CN} \longrightarrow \underset{\text{Acetic Acid}}{CH_3.CO_2H} \longrightarrow \underset{\text{Acetaldehyde}}{CH_3.CHO}$$

$$\longleftarrow$$

$$\underset{\text{Ethyl Alcohol}}{\underset{CH_3}{\overset{CH_2.OH}{|}}} \longrightarrow \underset{\text{Ethyl Iodide}}{\underset{CH_3}{\overset{CH_2I}{|}}} \longrightarrow \underset{\text{Ethyl Cyanide}}{\underset{CH_3}{\overset{CH_2CN}{|}}} \longrightarrow \underset{\text{Propionic Acid}}{\underset{CH_3}{\overset{CH_2CO_2H}{|}}} \longrightarrow \underset{\text{Propionic Aldehyde.}}{\underset{CH_3}{\overset{CH_2.CHO}{|}}} \quad \text{etc.}$$

Three reactions come into consideration in the breaking-down or decomposition of the normal fatty acids:

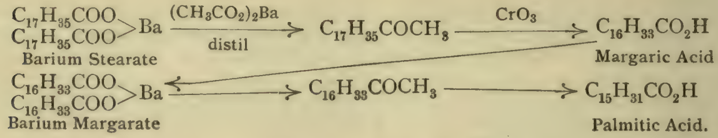
(1) The method of formation 8 (p. 243) of carboxylic acids: oxidation of mixed methyl-n-alkyl ketones, in which the CO-group continues in combination with the methyl group.

(2) The transformation 10 (p. 243) of acid amides by bromine and caustic potash.

(3) The action of iodine upon the silver salts.

The first of these three reactions F. Krafft employed in a systematic way for the breaking-down of stearic acid into normal fatty acids of known constitution, from which it was concluded that stearic acid and the lower homologues derived from it possessed normal constitution. Upon distilling *barium stearate*, $(C_{17}H_{35}CO_2)_2Ba$, and *barium acetate*, $(CH_3.CO_2)_2Ba$, *heptadecylmethyl ketone*, $C_{17}H_{35}COCH_3$, results. When this is oxidized it breaks down into *margaric acid*, $C_{16}H_{33}CO_2H$, and acetic acid. *Barium margarate* and barium acetate yield *hexadecylmethyl ketone*,

$C_{16}H_{33}.CO.CH_3$, and this, by oxidation, passes into *palmitic acid*, $C_{15}H_{31}CO_2H$, and acetic acid, etc.:



$$\begin{tikzcd}
\underset{\text{Barium Stearate}}{\substack{C_{17}H_{35}COO\\C_{17}H_{35}COO}>Ba} \arrow[r, "(CH_3CO_2)_2Ba", "\text{distil}"'] & C_{17}H_{35}COCH_3 \arrow[r, "CrO_3"] & \underset{\text{Margaric Acid}}{C_{16}H_{33}CO_2H} \arrow[dll] \\
\underset{\text{Barium Margarate}}{\substack{C_{16}H_{33}COO\\C_{16}H_{33}COO}>Ba} \arrow[r] & C_{16}H_{33}COCH_3 \arrow[r] & \underset{\text{Palmitic Acid.}}{C_{15}H_{31}CO_2H}
\end{tikzcd}$$

A. W. Hofmann (B. **19**, 1433) discovered the second method. It will be treated more fully in connection with the acid amides and nitriles (p. 266). The presentation of its course by diagram will only be given here. When the acid amides are treated with bromine and caustic potash they split off CO in the form of CO_2 and pass into the next lower primary amines, which by further treatment with the same reagents become the nitrile of a carboxylic acid containing an atom less of carbon, and its amide is still capable of a like transformation. By this method the higher, more easily obtained normal fatty acids can be transposed into lower acids:

$$\begin{tikzcd}
\underset{\text{Myristamide}}{C_{13}H_{27}CONH_2} \arrow[r] & \underset{\text{Tridecylamine}}{C_{13}H_{27}NH_2} \arrow[r] & \underset{\text{Tridecylnitrile}}{C_{12}H_{25}CN} \arrow[r] & \underset{\text{Tridecylamide.}}{C_{12}H_{25}CONH_2}
\end{tikzcd}$$

(4) Action of iodine upon silver salts: silver acetate yields, in addition to CO_2, the acetic methyl ester; silver capronate yields CO_2 and caproic amyl ester (B. **25**, R. 581; **26**, R. 237):

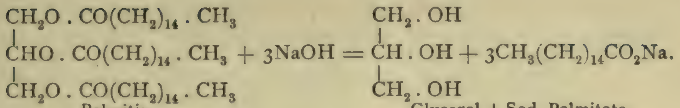
$$2CH_3CO_2Ag + I_2 = CH_3CO_2CH_3 + CO_2 + 2AgI.$$

TECHNICAL APPLICATION OF THE FATS AND OILS.

Animal fats, especially sheep-tallow and beef-tallow, the nature of which was made clear by the classic researches of Chevreul in the beginning of this century, consist mainly of a mixture of *glycerol esters* of *palmitic*, *stearic*, and *oleic acids*, which are commonly called palmitin, stearin, and olein. They have been used in the preparation of *artificial butter* (margarine), in the manufacture of *stearin candles*, *soaps*, and *plasters* from the acid residues present in them, and for the isolation of glycerol, which is used in part as such and in part in the form of *nitroglycerin*. Palm fat, cocoanut-oil, and olive oil are also used as raw material.

The so-called *stearin* of candles consists of a mixture of stearic and palmitic acids. For its preparation, beef-tallow and suet, both solid fats, are saponified with calcium hydroxide or sulphuric acid, or with superheated steam. The acids which separate are distilled with superheated steam. The yellow, semi-solid distillate, a mixture of stearic, palmitic, and oleic acids, is freed from the liquid oleic acid by pressing it between warm plates. The residual, solid mass is then fused together with some wax or paraffin, to prevent crystallization occurring when the mass is cold, and molded into candles.

When the fats are saponified by potassium or sodium hydroxide, salts of the fatty acids—*soaps*—are produced, *e.g.*, sodium palmitate, according to the equation:



$$\begin{array}{l} CH_2O\,.\,CO(CH_2)_{14}\,.\,CH_3 \\ | \\ CHO\,.\,CO(CH_2)_{14}\,.\,CH_3 \\ | \\ CH_2O\,.\,CO(CH_2)_{14}\,.\,CH_3 \end{array} + 3NaOH = \begin{array}{l} CH_2\,.\,OH \\ | \\ CH\,.\,OH \\ | \\ CH_2\,.\,OH \end{array} + 3CH_3(CH_2)_{14}CO_2Na.$$

Palmitin — Glycerol + Sod. Palmitate.

The sodium salts are solids and hard, while those with potassium are soft. Salt water will convert potash soaps into sodium soaps. In small quantities of water the salts of the alkalies dissolve completely, but with an excess of water they suffer decomposition, some alkali and fatty acid being liberated. The action of soap depends on this fact (B. **29**, 1328). The remaining metallic salts of the fatty acids are sparingly soluble or insoluble in water, but generally dissolve in alcohol. The lead salts, formed directly by boiling fats with litharge and water, constitute the so-called *lead plaster*.

The natural fats almost invariably contain several fatty acids (frequently, too, oleic acid). To separate them, the acids are set free from their alkali salts by means of hydrochloric acid and then fractionally crystallized from alcohol. The higher, less soluble acids separate out first. The separation is more complete if the acids be fractionally precipitated. The free acids are dissolved in alcohol, saturated with ammonium hydroxide, and an alcoholic solution of magnesium acetate added. The magnesium salt of the higher acid will separate out first; this is then filtered off and the solution again precipitated with magnesium acetate. The acids obtained from the several fractions are subjected anew to the same treatment, until, by further fractionation, the melting point of the acid remains constant—an indication of purity. The melting point of a mixture of two fatty acids is usually lower than the melting points of both acids (the same is the case with alloys of the metals).

Lanoline, or wool fat, is used in medicine.

DERIVATIVES OF THE ACIDS.

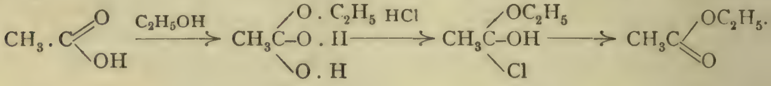
1. ESTERS OF THE FATTY ACIDS.

The esters of organic acids resemble those of the mineral acids in all respects (p. 136), and are prepared by analogous methods.

Methods of Formation.—(1) By direct action of acids and alcohols, whereby water is formed at the same time:

$$C_2H_5\,.\,OH + C_2H_3O\,.\,OH = C_2H_5\,.\,O\,.\,C_2H_3O + H_2O.$$

This transposition, as already stated, only takes place slowly (p. 137); heat hastens it, but it is never complete. If a mixture of like equivalents of alcohol and acid be employed, there will occur a time in the action when a condition of equilibrium will prevail, when the ester formation will cease, and both acid and alcohol will be simultaneously present in the mixture. This ensues because the heat modulus of the reaction is very slight, and hence, in accordance with the principles of thermochemistry, and under slightly modified conditions, the reaction pursues a reverse course—*i. e.*, the ester is decomposed by more water into alcohol and acid, since heat is generated when they are dissolved by the water. Both reactions mutually limit themselves. With excess of alcohol, more acid can be changed to ester, and with excess of acid more alcohol. The formation of the esters is more complete and rapid if the reaction products are assiduously withdrawn from the mixture. This may be effected either by distillation (providing the ester is readily volatilized), or by combining the water formed with sulphuric or hydrochloric acid, when the heat modulus will be appreciably augmented (A. **211**, 208). The action of the alcohol upon the carboxyl group may be supposed to take place in that at first there is an addition of alcohol, with the formation of a monoalkyl ether of the ortho-acid, and subsequently a splitting-off of water. The hydrochloric acid facilitates this in that it rearranges itself with the ortho-acid. The resulting chloride then decomposes spontaneously into the ester and hydrochloric acid (Henry, B. **10**, 2041):



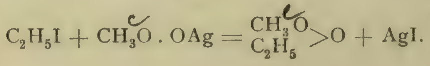
We practically have from the above the following methods of preparation: (*a*) Distil the mixture of the acid or its salt with alcohol and sulphuric acid. (*b*) Or, when the esters volatilize with difficulty, the acid or its salt is dissolved in excess of alcohol (or the alcohol in the acid), and while applying heat, HCl gas is conducted into the mixture (or H_2SO_4 added), and the ester precipitated by the addition of water. (*c*) The acid nitriles can be directly converted into esters by dissolving them in alcohol and heating them with dilute sulphuric acid (p. 267). In the case of many acids, a low percentage of alcoholic hydrochloric acid has shown itself as particularly well adapted for esterification purposes (B. **28**, 3201, 3215, 3252; compare esters of aromatic carboxylic acids).

Berthelot has executed more extended investigations upon the *ester* formation. These are of great importance to chemical dynamics. Proceeding from the simple assumption that the quantities of alcohol and acid combining in a unit of time (speed of reaction) are proportional to the product of the reacting masses, whose quantity regularly diminishes, Berthelot has proposed a formula (*Annalen chim. phis.*, 1862) by which the speed of the reaction in every moment of time, and its extent, can be calculated. van't Hoff has deduced a similar formula (B. **10**, 669), which Guldberg-Waage and Thomsen pronounce available for all limited reactions (*ibid.*, **10**, 1023). For a tabulation of the various calculations relating to this matter, see B. **17**, 2177; **19**, 1700. Of late, Menschutkin has extended the investigations upon ester formations to the several homologous series of acids and alcohols (A. **195**, 334, and **197**, 193; B. **15**, 1445 and 1572; **21**, R. 41). It has been found that the normal, primary alcohols (methyl alcohol excepted) possess the same speed of reaction. The exception is more reactive than the others. The secondary alcohols are esterified more slowly, and in the case of the tertiary alcohols this process proceeds very sluggishly. Formic acid is more reactive than acetic, and the latter more so than the succeeding homologues, with which the speed of esterification diminishes as the molecule grows larger. In acids where a primary alkyl is in union with carboxyl, the initial velocity is the greatest, those with secondary alkyls are less, and the lowest initial velocity is observed with acids having a tertiary alkyl.

The following are noteworthy methods of formation:

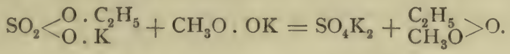
(2) Rearrangement of the alkyl esters of mineral acids with salts of the organic acids:

(*a*) By the action of the alkylogens (I) upon salts (Ag) of the acids:



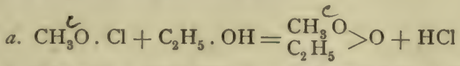
$$C_2H_5I + CH_3\overset{c}{\vphantom{O}}O\,.\,OAg = \begin{matrix} CH_3\overset{c}{\vphantom{O}}O \\ C_2H_5 \end{matrix}\!>O + AgI.$$

(*b*) By the dry distillation of a mixture of the alkali salts of the fatty acids and salts of alkyl sulphates:



$$SO_2<\begin{matrix}O\,.\,C_2H_5\\O\,.\,K\end{matrix} + CH_3O\,.\,OK = SO_4K_2 + \begin{matrix}C_2H_5\\CH_3O\end{matrix}>O.$$

(3) By the action of *acid chlorides* (p. 257) or *acid anhydrides* (p. 257) on the alcohols or alcoholates:



$$a.\ CH_3\overset{c}{}O\,.\,Cl + C_2H_5\,.\,OH = \begin{matrix}CH_3\overset{c}{}O\\C_2H_5\end{matrix}>O + HCl$$

$$b.\ C_2H_5OH + (CH_3CO)_2O = CH_3COOC_2H_5 + CH_3COOH.$$

(4) Electrosyntheses of monocarboxylic esters (p. 240).

Properties.—Usually, the esters of fatty acids are volatile, neutral liquids, soluble in alcohol and ether, but generally insoluble in water. Many of them possess an agreeable fruity odor, are prepared in large quantities, and find extended application as *artificial fruit essences.* Nearly all fruit-odors may be made by mixing the different esters. The esters of the higher fatty acids occur in the natural varieties of wax.

Consult B. **14**, 1274; A. **218**, 337; **220**, 290, 319; **223**, 247, upon the boiling points, the specific gravities and specific volumes of the fatty acid esters.

Transformations.—(1) When the esters are heated with water they sustain a partial decomposition into alcohol and acid. This decomposition (*saponification*) (p. 112) is more rapid and complete on heating with alkalies in alcoholic solution:

$$C_2H_3O\,.\,O\,.\,C_2H_5 + KOH = C_2H_3O\,.\,OK + C_2H_5\,.\,OH.$$

Consult A. **228**, 257, and **232**, 103; B. **20**, 1634, upon the velocity of saponification by various bases.

(2) Ammonia changes the esters into amides (p. 262):

$$C_2H_3O\,.\,O\,.\,C_2H_5 + NH_3 = C_2H_3\,.\,O\,.\,NH_2 + C_2H_5\,.\,OH.$$

(3) The haloid acids convert the esters into acids and haloid-esters (A. **211**, 178):

$$C_2H_3O\,.\,O\,.\,C_2H_5 + HI = C_2H_3O\,.\,OH + C_2H_5I.$$

(4) By the action of PCl_5 the extra-radical oxygen is replaced by chlorine, and both radicals are converted into halogen derivatives. Compare *oxalic ester* for the course of this reaction:

$$C_2H_3O\,.\,O\,.\,C_2H_5 + PCl_5 = C_2H_3O\,.\,Cl + C_2H_5Cl + POCl_3.$$

(5) The esters, containing alcohol radicals with high molecular weight, break down, when heated or distilled under pressure, into fatty acids and *olefines* (p. 92).

Esters of Acetic Acid.—The *Methyl Ester*, Methyl Acetate, $C_2H_3O_2\,.\,CH_3$, occurs in crude wood-spirit, boils at 57.5°, and has a specific gravity of 0.9577 at 0°. When chlorine acts upon it the alcohol radical is first substituted: $C_2H_3O_2\,.\,CH_2Cl$ boils at 150°; $C_2H_3O_2\,.\,CHCl_2$ boils at 148°.

The *Ethyl Ester*, Ethyl Acetate—Acetic Ether—$C_2H_3O_2\,.\,C_2H_5$, boils at 77°. At 0° its sp. gr. equals 0.9238. It is technically prepared from acetic acid, alcohol, and sulphuric acid. It is the officinal *Æther aceticus.* It is the starting-point for the production of *acetoacetic ester*, $CH_3 . CO . CH_2 . CO_2 . C_2H_5$, a factor in the formation of *antipyrine*.

Chlorine produces substitution products of the alcohol radicals. The n-*propyl ester* boils at 101°. The *isopropyl ester* boils at 91°.

n-*Butyl ester* boils at 124°. The *isobutyl ester* boils at 116°, the secondary *butyl ester* at 111°, and the tertiary at 96°.

The *Amyl Ester* boils at 148°; n-propyl-methyl carbinol acetate, $(CH_3CH_2CH_2)(CH_3)CHO . CO . CH_3$, at 133°, and isopropyl methyl carbinol acetate at 125°. At 200° it splits up into amylene and acetic acid. *Isobutyl carbinol acetate*, the acetic ester of amyl alcohol of fermentation, boils at 140°. A dilute alcoholic solution of it has the odor of pears, and is used as *pear oil*.

Acetic-n-*Hexyl Ester* occurs in the oil of *Heracleum giganteum*. It boils at 169–170° and possesses a fruit-like odor. *Acetic*-n-*octyl ester* is also present in the oil of *Heracleum giganteum*. It boils at 207° and has the odor of oranges.

The *allyl-ester* boils at 98–100°.

For higher acetic esters, see A. **233**, 260.

Orthoacetic Ester, $CH_3 . C(O . C_2H_5)_3$, boiling at 132°, is produced on warming *a-trichlorethane* or *methyl chloroform*, $CH_3 . CCl_3$ (p. 103), with sodium ethylate in ethereal solution.

Furthermore, the addition products of the *aldehydes* and acetic anhydride are the *acetic esters* (p. 191) of those glycols not capable of existing in a free condition. The aldehydes are probably the anhydrides of these bodies.

Later, in the presentation of the polyhydric alcohols their acetic esters will always be mentioned, for by their saponification a clue can be obtained as to the number of hydroxyl groups present in the alcohol.

Esters of Propionic Acid.—The *methyl ester* boils at 79.5°. The *ethyl ester* boils at 98.8°. The n-*propyl ester* boils at 122°; the *isobutyl ester* at 137°; and the *isoamyl ester* at 160°; the latter has an odor like that of pine-apples. (See A. **233**, 253.)

Esters of n-Butyric Acid.—*Methyl Ester* boils at 102.3°, and has an odor like that of rennet. The *ethyl ester* boils at 120.9°, has a pine-apple-like odor, and is employed in the manufacture of artificial rum. Its alcoholic solution is the artificial *pine-apple oil*.

The n-*propyl ester* boils at 143°; the *isopropyl ester* at 128°. The *isobutyl ester* boils at 157°. The *isoamyl ester* boils at 178°, and its odor resembles that of pears. The n-*hexyl ester*, boiling at 205°, and n-*octyl ester*, boiling at 244°, are found in the oil obtained from various species of *Heracleum* (see above) and the *octyl ester* in *Pastinaca sativa* (A. **163**, 193; **166**, 80; **233**, 272).

Methyl Isobutyric Ester boils at 92.3°. *Ethyl Isobutyric Ester*, $C_4H_7O_2 . C_2H_5$, boils at 110°. n-*Propyl Ester* boils at 135° (A. **218**, 334).

Esters of the Valeric Acids.—n-*Valeric Ethyl Ester* boils at 144° (A. **233**, 274). i-*Valeric Ethyl Ester* boils at 135°. i-*Valeric Isoamyl Ester* boils at 194°.

Methyl-ethyl Acetic Ethyl Ester boils at 133.5° (A. **195**, 120). *Trimethyl Acetic Ethyl Ester* boils at 118° (A. **173**, 372).

Esters of the Hexoic Acids.—n-*H.-ethyl ester* boils at 167°. *Isobutylacetic Ethyl Ester* boils at 161°.

n-**Heptoic Ethyl Ester** boils at 187–188°. n-**Octoic Ethyl Ester** boils at 207–208° (A. **233**, 282). n-**Nonoic Ethyl Ester** boils at 227–228°. n-**Caproic Ethyl Ester** boils with decomposition, at 275–290°; it is the principal constituent of the fusel oil of wine.

Lauric Ethyl Ester boils at 269°. **Myristic Ethyl Ester** melts at 10–11°, and boils at 295°.

Spermaceti and the Waxes.

Some of the esters with high molecular weights occur already formed in spermaceti and the waxes. This fact has been noted in connection with the corresponding alcohols and acids. The waxes are distinguished from the fats in that they consist of esters of monohydric alcohols with high molecular weight, whereas the fats are the esters of the *trihydric* alcohol, *glycerol*. Spermaceti belongs to the wax variety.

Spermaceti (*Cetaceum, Sperma Ceti*) occurs in the oil from peculiar cavities in the heads of whales (particularly *Physeter macrocephalus*), and upon standing and cooling it separates as a white crystalline mass, which can be purified by pressing and recrystallization from alcohol. It consists of **Cetyl Palmitic Ester,** $C_{16}H_{31}O_2 . C_{16}H_{33}$, which crystallizes from hot alcohol in waxy, shining needles or leaflets, and melts at 49°. It volatilizes undecomposed in a vacuum. Distilled under pressure, it yields *hexadecylene* and *palmitic acid*. When boiled with alcoholic caustic potash it becomes palmitic acid and cetyl alcohol.

Ordinary beeswax is a mixture of cerotic acid, $C_{27}H_{54}O_2$, with **Myricyl Palmitic Ester,** $C_{16}H_{31}O_2 . C_{30}H_{61}$. Boiling alcohol extracts the cerotic acid and the ester ***myricin*** remains (A. **224,** 225).

Consult A. **235,** 106, for other constituents of beeswax.

Carnaüba wax, from the leaves of the carnuba tree, melts at 83°. It contains free ceryl alcohol and various acid esters (A. **223,** 283).

Chinese wax is **Ceryl Cerotic Ester,** $C_{27}H_{53}O_2 . C_{27}H_{55}$. Alcoholic potash decomposes it into cerotic acid and ceryl alcohol.

2. ACID HALOIDS, OR HALOID ANHYDRIDES OF THE FATTY ACIDS.

The haloid anhydrides of the acids (or acid haloids) are those derivatives which arise in the replacement of the hydroxyl of acids by halogens; they are the halogen compounds of the acid radicals. They have been termed haloid anhydrides, because they can be viewed as *mixed anhydrides* (p. 259) of the fatty acids and the haloid acids, corresponding to the method of formation (1) of the acid chlorides.

Acid Chlorides.—(1) From fatty acids and hydrochloric acid, by means of P_2O_5:

$$CH_3 . COOH + HCl \xrightarrow{P_2O_5} CH_3 . COCl + H_2O.$$

(2) By the action of hydrochloric acid gas upon a mixture of an acid nitrile and a carboxylic acid or an anhydride at 0°. The hydrochloride of the acid amide is produced at the same time (B. **29,** R. 87):

$$CH_3CN + CH_3 . COOH + 2HCl = CH_3 . CONH_2 . HCl + CH_3 . COCl.$$

(3) By the action of chlorine upon aldehydes:

$$CH_3 . COH + Cl_2 = CH_3 . COCl + HCl.$$

(4) A far more important method of formation consists in letting

the phosphorus haloids act upon the acids or their salts—just as the alkylogens are produced from the alcohols (p. 139):

$$\begin{aligned}(a)\quad & CH_3 . COOH + PCl_5 = CH_3 . COCl + POCl_3 + HCl\\ (b)\quad & 3CH_3 . COOH + PCl_3 = 3CH_3 . COCl + PO_3H_3\\ (c)\quad & 2CH_3 . COONa + POCl_3 = 2CH_3 . COCl + PO_3Na + NaCl.\end{aligned}$$

Should there be an excess of the salt, the acid will also act upon it and acid anhydrides result (p. 259). The action, particularly upon the salts, is very violent.

(5) Carbon oxychloride and thionyl chloride (see malonyl chloride) act upon the free acids and their salts the same as the chlorides of phosphorus. Acid chlorides and anhydrides are produced. This method has met with technical application (B. **17**, 1285; **21**, 1267):

$$C_2H_3O . OH + COCl_2 = C_2H_3OCl + CO_2 + HCl.$$

(6) Acid chlorides are also produced by the interaction of phosgene and zinc alkyls (p. 240).

Historical.—Liebig and Wöhler obtained the first acid choride in 1832, when they treated benzaldehyde, C_6H_5COH, with chlorine. It was *benzoyl chloride*. C_6H_5-COCl, the chloride of the simplest aromatic acid—benzoic acid. In 1846, Cahours discovered the method of producing aromatic acid chlorides by the action of phosphorus pentachloride upon monocarboxylic acids. *Acetyl chloride* was first prepared in 1851 by Gerhardt (A. **87**, 63) by treating sodium acetate with phosphorus oxychloride.

Acid Bromides.—(1) The phosphorus bromides act like the corresponding chlorides upon the fatty acids or their salts. A mixture of amorphous phosphorus and bromine may be employed as a substitute for the prepared bromide.

(2) An interesting method for preparing the acid bromides consists in letting air act upon certain bromide derivatives of the alkylens, whereby oxygen will be absorbed. An intramolecular atomic rearrangement (p. 52) takes place (B. **13**, 1980; **21**, 3356):

Unsym. Dibromethylene, $CH_2 = CBr_2 \xrightarrow{O} CH_2Br . COBr$, Bromacetyl Bromide.

Tribromethylene, $CHBr = CBr_2 \xrightarrow{O} CHBr_2 . COBr$, Dibromacetyl Bromide.

Acid Iodides.—Phosphorus iodide does not convert the acids into iodides of the acid radicals; this only occurs when the acid anhydrides are employed. They are also produced by the interaction of acid chlorides and calcium iodide.

Acid Fluorides.—*Acetyl Fluoride* is a gas with an odor resembling that of phosgene. It is formed in the action of AgF or AsF_3 upon acetyl chloride. A better procedure consists in allowing acid chlorides to act upon anhydrous zinc fluoride.

Propionyl Fluoride, $CH_3 . CH_2 . COF$, boils at 44°.

Properties and Transpositions.—The acid haloids are sharp-smelling liquids, which fume in the air. They are heavier than water, sink in it, and at ordinary temperatures (1) decompose, forming acids and halogen hydrides. The more readily soluble the resulting acid is in water, the more energetic will the reaction be.

The acid chlorides act similarly upon many other bodies. (2) They yield compound ethers, or esters, with the alcohols or alcoholates (p. 253). (3) With salts or acids they yield acid anhydrides (p. 259), and (4) with ammonia, the amides of the acids, etc.

(5) Sodium amalgam, or better, sodium and oxalic acid (B. **2**, 98), will convert the acid chlorides into *aldehydes* and alcohols (pp. 190

and 113). (6) They yield ketones and tertiary alcohols when treated with the zinc alkyls (pp. 209 and 113). (7) By the action of silver cyanide they pass into the *acid cyanides*, which are described as the nitriles of the α-ketone carboxylic acids. (8) Di- and poly carboxylic acids, having the power of forming anhydrides, pass when treated with acid chlorides (especially acetyl chloride) into their anhydrides.

Acetyl Chloride [Ethanoyl Chloride], $CH_3 . CO . Cl$, boils at 55°. It is formed according to the general methods applied in the production of acid chlorides, and by carefully distilling a mixture of acetic acid (3 parts) and PCl_3 (2 parts). Or, heat $POCl_3$ (2 molecules) with acetic acid (3 molecules), as long as HCl escapes, then distil (A. **175**, 378). The acetyl chloride is purified by again distilling over a little dry sodium acetate. It is a colorless, pungent-smelling liquid which has a specific gravity of 1.130 at 0°. Water decomposes it very energetically. For its transformations, consult the preceding paragraphs.

Acetyl chloride forms chlorinated acetic acids with chlorine. Compare acetyl acetone.

Acetyl Bromide boils at 81°.

Acetyl Iodide boils at 108°.

Propionyl Chloride, $CH_3 . CH_2 . CO . Cl$, boils at 80°; the *bromide*, at 104°, and the *iodide* at 127°.

Butyryl Chloride, $C_4H_7O . Cl$, boils at 101°. Aluminium chloride changes it to triethylphloroglucin (B. **27**, R. 507). The n-*bromide* boils at 128°; the n-*iodide* at 146–148°. Sodium amalgam converts it into normal butyl alcohol. **Isobutyryl Chloride,** $(CH_3)_2 . CH . CO . Cl$, boils at 92°; the *bromide* at 116–118°.

Isovaleryl Chloride, $C_5H_9O . Cl$, boils at 113.5–114.5°; the *bromide* at 143°, and the *iodide* at 168°

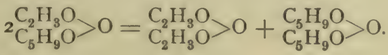
Trimethyl Acetic Chloride, $(CH_3)_3C . COCl$, boils at 105–106°. n-*Caproyl Chloride*, $CH_3(CH_2)_4COCl$, boils at 151–153°. *Diethylacetyl Chloride*, $(C_2H_5)_2CHCOCl$, boils at 134–137°. *Dimethyl-ethyl acetic chloride*, $(CH_3)_2(C_2H_5)C . COCl$, boils at 132°.

Consult B. **17**, 1378; **19**, 2982; **23**, 2384, for the chlorides of the higher fatty acids.

3. ACID ANHYDRIDES.

The acid anhydrides are the oxides of the acid radicals. In those of the monobasic acids two acid radicals are united by an oxygen atom; they are analogous to the oxides of the univalent alcohol radicals—the ethers.

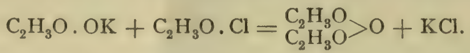
The *simple* anhydrides, those containing two *similar* radicals, can as a general thing be distilled, while the *mixed* anhydrides, with two dissimilar radicals, decompose when thus treated, into two simple anhydrides:



$$2\begin{matrix}C_2H_3O\\C_5H_9O\end{matrix}>O = \begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}>O + \begin{matrix}C_5H_9O\\C_5H_9O\end{matrix}>O.$$

Hence they are not separated from the product of the reaction by distillation, but are dissolved out with ether.

Methods of Formation.—(1*a*) The chlorides of the acid radicals are allowed to act on anhydrous salts—viz., the alkali salts of the acids:



$$C_2H_3O.OK + C_2H_3O.Cl = \begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}{>}O + KCl.$$

(1*b*) The anhydrides of the higher fatty acids can be produced further by the action of acetyl chloride on the latter (B. **10**, 1881).

(2) Phosphorus oxychloride (1 molecule) acts upon the dry alkali salts of the acids (4 molecules). The acid chloride which appears in the beginning acts immediately upon the excess of salt:

$$\begin{aligned}\text{I Phase: } & 2C_2H_3O.OK + POCl_3 &&= 2C_2H_3O.Cl + PO_3K + KCl\\ \text{II Phase: } & C_2H_3O.OK + C_2H_3O.Cl &&= (C_2H_3O)_2O + KCl.\end{aligned}$$

(3) Phosgene, $COCl_2$, acts like $POCl_3$. In this reaction acid chlorides are also produced (p. 258).

(4) A direct conversion of the acid chlorides into the corresponding anhydrides may be effected by permitting the former to act upon anhydrous oxalic acid (A. **226**, 14):

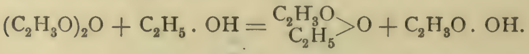
$$2C_2H_3OCl + C_2O_4H_2 = (C_2H_3O)_2O + 2HCl + CO_2 + CO.$$

Historical.—Charles Gerhardt (1851) discovered the acid anhydrides. The important bearing of this discovery upon the *type theory* has already been alluded to in the introduction.

Properties and Deportment.—The acid anhydrides are liquids or solids of neutral reaction, and are soluble in ether. Their boiling points are *higher* than those of the corresponding acids. (1) Water decomposes them into their constituent acids:

$$(C_2H_3O)_2O + H_2O = 2C_2H_3O.OH.$$

(2) With alcohols they yield the esters:



$$(C_2H_3O)_2O + C_2H_5.OH = \begin{matrix}C_2H_3O\\C_2H_5\end{matrix}{>}O + C_2H_3O.OH.$$

(3) Ammonia and primary and secondary amines convert them into amides and ammonium salts:

$$(CH_3CO)_2O + 2NH_3 = CH_3.CONH_2 + CH_3.COONH_4.$$

(4) Heated with hydrochloric acid, hydrobromic and hydriodic acids, they decompose into an acid haloid and free acid:

$$(C_2H_3O)_2O + HCl = C_2H_3O.Cl + C_2H_3O.OH.$$

(5) Chlorine splits them up into acid chlorides and chlorinated acids:

$$(C_2H_3O)_2O + Cl_2 = C_2H_3O.Cl + Cl.CH_2.COOH.$$

(6) Sodium amalgam changes the anhydrides to aldehydes and primary alcohols.

(7) Aldehydes and acid anhydrides combine to esters.

Acetic Anhydride [Ethan-acid Anhydride], $(C_2H_3O)_2O$, is a mobile, pungent-smelling liquid boiling at 137°. Its specific gravity equals 1.073 at 0°.

To prepare it, distil a mixture of anhydrous sodium acetate (3 parts) with phosphorus oxychloride (1 part); or, better, employ equal quantities of the salt and acetyl chloride.

Propionic Anhydride, $(C_3H_5O)_2O$, boils at 168°. **Butyric Anhydride** boils at 191–193°.

Isobutyric Anhydride boils at 181.5°. n-*Caproic Anhydride* boils with decomposition at 241–243°. *Œnanthic Anhydride* boils at 258° with partial decomposition. *Pelargonic Anhydride* melts at +5° and *palmitic anhydride* at 64°.

4. ACID PEROXIDES.

The peroxides of the acid radicals are produced on digesting the chlorides or anhydrides in ethereal solution with barium peroxide (Brodie, Pogg. Ann., **121**, 382) or by the action of ice-cold chlorides upon hydrated sodium peroxide (B. **29**, 1726):

$$2C_2H_3O\,.\,Cl + BaO_2 = (C_2H_3O)_2O_2 + BaCl_2.$$

Acetyl Peroxide is a thick liquid, insoluble in water, but readily dissolved by alcohol and ether. It is a very unstable, strong, oxidizing agent, separating iodine from potassium iodide solutions and decolorizing a solution of indigo. Sunlight decomposes it, and when heated it explodes violently. With barium hydroxide it yields barium acetate and barium peroxide.

5. THIO-ACIDS.

By the replacement of oxygen in a monocarboxylic acid by sulphur three cases are possible:

1. $R'.CO.SH$ Thio-acids [Thiolic Acids]
2. $R'.CS.OH$ Thionic Acids, compare Thiamides
3. $R'.CS.SH$ Dithionic Acids [Thionthiolic Acids].

Aliphatic acids of the first kind alone are known. The first thio-acid—*thiacetic acid*, $CH_3.COSH$,—was obtained by Kekulé (A. **90**, 309) when phosphorus pentasulphide acted upon acetic acid. It is advisable to mix the P_2S_5 with half its weight of coarse pieces of glass:

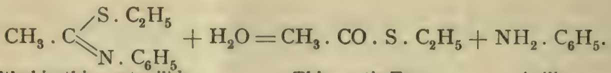
$$5C_2H_3O\,.\,OH + P_2S_5 = 5C_2H_3O\,.\,SH + P_2O_5.$$

The *thio-anhydrides* arise in the same manner by the action of phosphorus sulphide upon the acid anhydrides. The thio acids are produced by the action of acid chlorides upon potassium sulphydrate. The disagreeably-smelling thio-acids correspond to the thio-alcohols or mercaptans (p. 149), their *sulphanhydrides* to the acid anhydrides and the simple sulphides, and their *disulphides* to the peroxides and alkyl disulphides:

$CH_3.CH_2SH$ Ethyl Mercaptan	$CH_3.COSH$ Thiacetic Acid	$CH_3.CO_2H$ Acetic Acid
$(CH_3.CH_2)_2S$ Ethyl Sulphide	$(CH_3.CO)_2S$ Thiacetic Anhydride	$(CH_3CO)_2O$ Acetic Anhydride
$(CH_3.CH_2)_2S_2$ Ethyl Disulphide	$(CH_3.CO)_2S_2$ Acetyl Disulphide	$(CH_3.CO)_2O_2$ Acetyl Peroxide.

The *esters* are obtained when the alkylogens react with the salts of the thio-acids, and by letting the acid chlorides act upon the mercaptans or mercaptides.

They also appear in the decomposition of alkylic isothio-acetanilides with dilute hydrochloric acid:



$$CH_3 . C\begin{matrix}\diagup S . C_2H_5\\ \diagdown N . C_6H_5\end{matrix} + H_2O = CH_3 . CO . S . C_2H_5 + NH_2 . C_6H_5.$$

Ethyl-isothio-acetanilide Thio-acetic Ester Aniline.

Concentrated caustic potash decomposes the esters into fatty acids and mercaptans.

Thiacetic Acid [*Ethaniol-acid*], CH_3COSH, is a colorless liquid, boiling at 93°. Its specific gravity at 10° is 1.074. Its odor resembles those of acetic acid and hydrogen sulphide. It dissolves with difficulty in water, but readily in alcohol and in ether. This acid has been recommended as a very convenient substitute for hydrogen sulphide in analytical operations (B. **28**, R. 616). The *lead salt*, $(C_2H_3O . S)_2Pb$, crystallizes in minute needles, and readily decomposes with the formation of lead sulphide. The *ethyl ester*, $C_2H_3O . S . C_2H_5$, boils at 115°.

Acetyl Sulphide, $(C_2H_3O)_2S$, is a heavy, yellow oil, insoluble in water. It boils at 157°. Water gradually decomposes it into acetic and thiacetic acids (B. **24**, 3548, 4251).

Acetyl Disulphide, $(C_2H_3O)_2S_2$, is formed when acetyl chloride acts upon potassium disulphide, or iodine upon the salts of the thio-acid.

6. ACID AMIDES.

These correspond to the amines of the alcohol radicals. The hydrogen of ammonia can be replaced by acid radicals, forming primary, secondary and tertiary acid amides:

$CH_3 . CO . NH_2$ Acetamide (primary)

$(CH_3 . CO)_2NH$ Diacetamide (secondary)

$(CH_3 . CO)_3N$ Triacetamide (tertiary).

Recently the idea has been expressed that the constitution of the primary acid amides might be represented by the formula $R'. C\begin{matrix}\diagup OH\\ \diagdown NH\end{matrix}$ (compare benzamide), from which the imido-ethers (p. 269) are derived.

The hydrogen of primary and secondary amines, like that of ammonia, can be replaced by acid residues, giving rise to *mixed amides.*

General Methods of Formation.—(1) The dry distillation of the ammonium salts of the acids of this series. A more abundant yield is obtained by merely heating the ammonium salts to about 230° (B. **15**, 979), (Kündig, 1858). (This method was first applied (1830) by Dumas to ammonium oxalate with the production of oxamide). This procedure is adapted to the preparation of volatile amides:

$$C_2H_3O . O . NH_4 = C_2H_3O . NH_2 + H_2O.$$

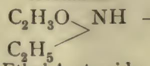
Ammonium Acetate Acetamide.

A mixture of the sodium salts and ammonium chloride may be substituted for the ammonium salts. Consult B. **17**, 848, upon the velocity and limit of the amide production.

(2) The action of ammonia, primary and secondary amines upon

the esters (by this procedure Liebig, in 1834, obtained oxamide from oxalic ester):

$$CH_3CO.O.C_2H_5 + NH_3 = \underset{\text{Acetamide}}{CH_3CO.NH_2} + C_2H_5.OH$$



$$CH_3CO.O.C_2H_5 + C_2H_5.NH_2 = \underset{\text{Ethyl Acetamide.}}{{}^{C_2H_3O}_{C_2H_5}\!\!>NH} + C_2H_5.OH.$$

This is a reaction that frequently takes place in the cold; it is best, however, to apply heat to the alcoholic solution.

It is one of the so-called reversible reactions, inasmuch as the action of alcohols upon acid amides again produces esters and ammonia (B. **22**, 24).

(3) By the action (*a*) of *acid haloids*, (*b*) of *acid anhydrides* upon ammonia, primary and secondary alkylamines. (This method Liebig and Wöhler first used in 1832 to prepare benzamide from benzoyl chloride.):

$$(3a)\ CH_3.COCl + 2NH_3 = \underset{\text{Acetamide}}{CH_3.CONH_2} + NH_4Cl$$

$$CH_3.COCl + 2NH_2C_2H_5 = \underset{\text{Ethyl Acetamide}}{CH_3.CONH.C_2H_5} + N(C_2H_5)HCl$$

$$CH_3.COCl + 2NH(C_2H_5)_2 = \underset{\text{Diethyl Acetamide.}}{CH_3.CON(C_2H_5)_2} + N(C_2H_5)_2H_2Cl.$$

This method is especially well adapted for obtaining the amides of the higher fatty acids (B. **15**, 1728):

$$(3b)\ (CH_3.CO)_2O + 2NH_3 = CH_3.CONH_2 + CH_3.CO_2NH_4$$

$$(CH_3.CO)_2O + 2NH_2C_2H_5 = CH_3.CONHC_2H_5 + CH_3.CO_2NH_3C_2H_5.$$

(4) The addition of one molecule of water to the nitriles of the acids:

$$\underset{\text{Acetonitrile}}{CH_3.CN} + H_2O\ (180°) = \underset{\text{Acetamide.}}{CH_3.CO.NH_2.}$$

This addition of water frequently occurs in the cold by the action of concentrated hydrochloric acid, or by mixing the nitrile with glacial acetic acid and concentrated sulphuric acid (B. **10**, 1061). Hydrogen peroxide in alkaline solution also converts the nitriles, with liberation of oxygen, into amides (B. **18**, 355). For the action of hydrochloric acid upon a mixture of nitrile and fatty acid see (2) formation of acid chlorides.

(5) The distillation of the fatty acids with potassium sulphocyanide:

$$2C_2H_3O.OH + CN.SK = C_2H_3O.NH_2 + C_2H_3O.OK + COS.$$

Simply heating the mixture is more practical (B. **16**, 2291; **15**, 978). In making acetamide glacial acetic acid and ammonium sulphocyanide are heated together for several days. In this reaction the aromatic acids yield nitriles.

(6) By the interaction of fatty acids and *carbylamines* (p. 236):

$$2CH_3.COOH + C:N.CH_3 = \underset{\text{Methyl Formamide.}}{H.CONHCH_3} + (CH_3CO)_2O.$$

(7) By the action of the fatty acids upon *isocyanic acid esters* (see these):

$$CH_3.COOH + CON.C_2H_5 = CH_3.CONHC_2H_5 + CO_2.$$

Secondary and *tertiary amides* are obtained (1) by heating primary acid amides (B. 23, 2394), the alkyl cyanides or nitriles with acids, or acid anhydrides, to 200°:

$$CH_3.CONH_2 + (CH_3CO)_2O = (CH_3.CO)_2NH + CH_3.COOH$$

$$CH_3CN + CH_3.COOH = (CH_3CO)_2NH$$

Diacetamide

$$CH_3.CN + (CH_3CO)_2O = (CH_3CO)_3N.$$

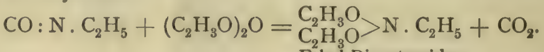
Triacetamide.

(2) The secondary amides can also be prepared by heating primary amides with dry hydrogen chloride:

$$2C_2H_3O.NH_2 + HCl = (C_2H_3O)_2NH + NH_4Cl.$$

Diacetamide.

(3) Mixed amides are further produced by the action of esters of ordinary isocyanic acid upon acid anhydrides:



$$CO:N.C_2H_5 + (C_2H_3O)_2O = \begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\!>N.C_2H_5 + CO_2.$$

Ethyl Diacetamide.

Properties and Behavior.—The amides of the fatty acids are usually solid, crystalline bodies, soluble in both alcohol and ether. The lower members are also soluble in water, and can be distilled without decomposition. As they contain the basic amido-group they are able to unite directly with acids, forming salt-like derivatives (*e. g.*, $C_2H_3O.NH_2.NO_3H$ and $(CH_3CO.NH_2)_2.HCl$), but these are not very stable, because the basic character of the amido-group is strongly neutralized by the acid radical. Furthermore, the acid radical imparts to the NH_2-group the power of exchanging a hydrogen atom with metals, *e. g.*, mercury or sodium (B. 23, 3037), forming metallic derivatives, *e. g.*, $(CH_3.CO.NH)_2.Hg$—mercury acetamide, analogous to the isocyanates (from isocyanic acid, CO : NH), and the salts of the imides of dibasic acids.

The union of the amido-group with the acid radicals (the group CO) is very feeble in comparison with its union with the alkyls in the amines (p. 159). The amides, therefore, readily absorb water and pass into ammonium salts, or acids and ammonia. (1) Heating with water effects this, although it is more easily accomplished by boiling with alkalies or acids. This is a reaction which is not infrequently termed *saponification* (p. 239).

$$CH_3.CO.NH_2 + H_2O = CH_3.CO.OH + NH_3.$$

Acid amides, saponifying with difficulty, are dissolved in sulphuric acid, and to this cold solution sodium nitrite is added (B. 28, 2783).

(2) Nitrous acid decomposes the primary amides similarly to the primary amines (p. 166):

$$C_2H_3O.NH_2 + NO_2H = C_2H_3O.OH + N_2 + H_2O.$$

(3) Bromine in alkaline solution changes the primary amides to bromamides (B. 15, 407 and 752):

$$C_2H_3O.NH_2 + Br_2 = C_2H_3O.NHBr + HBr,$$

which then form amines (p. 163). (4) On heating with phosphorus pentoxide, or with the chloride, they part with one molecule of water and become nitriles (cyanides of the alcohol radicals):

$$CH_3 . CO . NH_2 = CH_3 . CN + H_2O.$$

In this action a replacement of an oxygen atom by two chlorine atoms takes place; the resulting chlorides, like $CH_3 . CCl_2 . NH_2$, then lose, upon further heating, two molecules of ClH with the formation of nitriles.

Formamide, $H . CONH_2$. See p. 227.

Acetamide [Ethanamide], $CH_3CO . NH_2$, crystallizes in long needles, melts at 82–83°, and boils at 222° undecomposed. It dissolves with ease in water and alcohol. In explaining the methods of producing the amides, and in illustrating their deportment, acetamide was presented as the example. Dumas, Leblanc, and Malaguti first prepared it in 1847, by allowing ammonia to act upon acetic ester.

Acetmethylamide, $CH_3 . CONHCH_3$, melts at 28° and boils at 206°; *acetdimethylamide*, $CH_3 . CO . N(CH_3)_2$, boils at 165.5°; *acetethylamidé* boils at 205°; *acetdiethylamide* boils at 185–186°. *Methylene diacetamide*, $CH_2(NHCOCH_3)_2$, melts at 196° and boils at 288° (B. **25**, 310). *Chloralacetamide*, $CCl_3CH(OH)NHCOCH_3$, melts at 117° (B. **10**, 168). Acetamide and butylchloral yield two isomeric compounds melting at 158° and 170° respectively (B. **25**, 1690).

Diacetamide, $(C_2H_3O)_2NH$, is readily soluble in water, fuses at 77°, and boils at 222.5–223.5°. (Preparation, p. 264.)

Methyldiacetamide, $(CH_3CO)_2N . CH_3$, boils at 192°. *Ethyldiacetamide* boils at 185–192°.

Triacetamide, $(C_2H_3O)_3N$, melts at 78–79°. (Preparation, p. 264.)

Acetchloramide, $CH_3CONHCl$, melts at 110°.

Acetbromamide, $CH_3CONHBr + H_2O$, forms large plates, and melts in an anhydrous condition at 108° (B. **23**, 2395).

Higher homologous primary Acid Amides:

Propionamide melts at 75° and boils at 210°.

n-**Butyramide** fuses at 115° and boils at 216°. **Isobutyramide** fuses at 128° and boils at 216–220°.

n-**Valeramide** fuses at 114–116°.

Trimethylacetamide melts at 153–154° and boils at 212°; n-**Capronamide** melts at 100° and boils at 225°; **Methyl-n-propylacetamide** melts at 95°; **Methyl-isopropylacetamide** melts at 129°; **Isobutylacetamide** melts at 120°; **Diethylacetamide** melts at 105° and boils at 230–235°; **Œnanthamide** melts at 95° and boils at 250–258°; n-**Caprylamide** melts at 105-106°; **Pelargonamide** melts at 92–93°; n-**Caprinamide** melts at 98°.

Lauramide fuses at 102° and boils at 199–200° (12.5 mm.); **Tridecylamide** melts at 98.5°; **Myristamide**, at 102°, and boils at 217° (12 mm.); **Palmitamide**, at 106°, and boils at 235–236° (12 mm.); **Stearamide** melts at 108.5–109° and boils at 250–251° (12 mm.) (B. **15**, 977, 1729; **19**, 1433; **24**, 2781; **26**, 2840).

7. ACID HYDRAZIDES.

Acethydrazide, $CH_3 CO . NH . NH_2$, melts at 62°. *Acetbenzalhydrazine*, $CH_3 .- CO . NH . N : CH . C_6H_5$, melts at 134° (B. **28**, R. 242).

8. THE FATTY ACID NITRILES OR ALKYL CYANIDES.

These are compounds in which *one* carbon atom, combined with an alkyl group $R'.C\equiv$, a residue present in every fatty acid, replaces the three hydrogen atoms of ammonia, *e. g.*, $CH_3C\equiv N$, acetonitrile. It is true that in the *nitrile bases* (tertiary amines and amides) the nitrogen atom is also joined with three valences to carbon, but three alkyl residues are in union with *three* different carbon atoms.

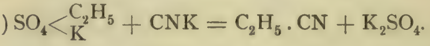
The acid nitriles are also called *alkyl cyanides*, because they can be viewed as *alkyl ethers* of hydrogen cyanide, $H.C\equiv N$.

Being intermediate steps in the synthesis of the fatty acids from the *alcohols*, these nitriles merit especial consideration.

The following general methods answer for their preparation:

(1) *Nucleus-synthesis* from the alcohols: (*a*) by heating the alkylogens with potassium cyanide in alcoholic solution to 100°; (*b*) by distillation of a potassium alkyl sulphate with potassium cyanide (hence the name *alkyl cyanides*):

(1*a*) $$C_2H_5I + CNK = C_2H_5.CN + KI$$

(1*b*) 

$$SO_4{<}\begin{matrix}C_2H_5\\K\end{matrix} + CNK = C_2H_5.CN + K_2SO_4.$$

Isocyanides (p. 235) form in slight amount in the first reaction. For their removal shake the distillate with aqueous hydrochloric acid until the unpleasant odor of the isocyanides has disappeared, then neutralize with soda and dry the nitriles with calcium chloride.

(2) By heating alkyl isocyanides or alkyl carbylamines (p. 237):

$$CH_3.CH_2.NC \xrightarrow{250^\circ} CH_3CH_2CN.$$

(3) The dry distillation of ammonium salts of the acids with P_2O_5, or some other dehydrating agent:

$$\underset{\text{Ammonium Acetate}}{CH_3.CO.O.NH_4} - 2H_2O = \underset{\text{Acetonitrile.}}{CH_3.CN.}$$

This method of production explains why these cyanides are termed acid nitriles. The corresponding acid amide is an intermediate product.

(4) By the removal of water from the amides of the acids when these are heated with P_2O_5, P_2S_5—or phosphoric chloride (see amidchlorides, p. 268):

$$CH_3.CO.NH_2 + PCl_5 = CH_3.CN + POCl_3 + 2HCl$$
$$5CH_3.CO.NH_2 + P_2S_5 = 5CH_3.CN + P_2O_5 + 5H_2S.$$

(5) Primary amines, containing more than five carbon atoms, are converted, by caustic potash and bromine, into nitriles:

$$C_7H_{15}CH_2NH_2 + 2Br_2 + 2KOH = C_7H_{15}CH_2NBr_2 + 2KBr + 2H_2O$$
$$C_7H_{15}CH_2NBr_2 + 2KOH = C_7H_{15}CN + 2KBr + 2H_2O.$$

As the primary amines can be obtained from acid amides containing a carbon atom more, these reactions will serve for the breaking-down of the fatty acids (p. 243).

(6) Nitriles result when aldoximes are heated with acetic anhydride or with thionyl chloride (B. **28**, R. 227):

$$CH_3CH = N.OH + (CH_3CO)_2O = CH_3C \equiv N + 2CH_3.COOH.$$

(7) On the application of heat to cyanacetic acid and alkylized cyanacetic acid nitriles result:

$$CN.CH_2.CO_2H = CN.CH_3 + CO_2.$$

The nitriles occur already formed in bone-oils.

Historical.—Pelouze (1834) discovered propionitrile on distilling barium ethyl sulphate with potassium cyanide (A. **10**, 249). Dumas (1847) obtained acetonitrile by distilling ammonium acetate alone, or with P_2O_5; the same occurred with the latter reagent and acetamide (p. 265). Dumas, Malaguti and Leblanc (A. **64**, 334) on the one hand, and Frankland and Kolbe (A. **65**, 269, 288, 299) on the other, demonstrated (1847) the conversion of the nitriles into their corresponding acids by means of caustic potash or dilute acids, and thus showed what importance the acid nitriles possessed for synthetic organic chemistry.

Properties and Behavior.—The nitriles are liquids, usually insoluble in water, possessing an ethereal odor, and distilling without decomposition.

Their reactions are based upon the easy disturbance of the triple union between nitrogen and carbon. They are mostly additive reactions. *Acid nitriles may be viewed as unsaturated compounds*, in the same sense as aldehydes and ketones (pp. 38, 187). Their neutral character distinguishes them from prussic acid, the nitrile of formic acid. In respect to this transposition of their C≡N-group they resemble the nitrile of formic acid.

(1) Nascent hydrogen converts them into primary amines (Mendius). This reduction is most easily accomplished by means of metallic sodium and absolute alcohol (B. **22**, 812).

(2) The nitriles can unite with the halogen hydrides, forming amide and imide haloids.

(3) Under the influence of concentrated sulphuric acid they take up water and become acid amides (p. 262). When heated to 100° with water the acid amides first formed absorb a second molecule of water and change to the fatty acid and ammonia. The nitriles are more readily saponified by heating them with alkalies or dilute acids (hydrochloric or sulphuric acid). Esters are produced when the acids, in a solution of absolute alcohol, act upon the nitriles.

(4) The nitriles form thiamides with H_2S (p. 269).

(5) They combine with alcohols and HCl to imido-ethers (p. 269).

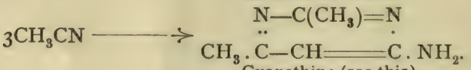
(6) With monobasic acids and acid anhydrides they yield secondary and tertiary amides (p. 264).

(7) The nitriles become amidines with ammonia and the amines (p. 270).

(8) Hydroxylamine unites with them to form amidoximes (p. 271). Metallic sodium induces in them peculiar polymerizations. In ethereal solution, dimolecular nitriles result: *imides* of *β-ketonic nitriles.* All these reactions depend upon the additive power of the nitriles, the triple carbon-nitrogen union being broken. If, however, sodium acts upon the pure nitriles at a temperature of 150° the products are *trimolecular nitriles,* so-called *cyanethines* (see these), *pyrimidine* derivatives:

$$2CH_3CN \longrightarrow CH_3.C(NH).CH_2.CN$$

Imido-acetic Nitrile



$$3CH_3CN \longrightarrow \begin{array}{l} \quad N{-}C(CH_3){=}N \\ CH_3.\ddot{C}{-}CH{=\!=}C.NH_2. \end{array}$$

Cyanethine (see this).

Acetonitrile, *Methyl Cyanide* [Ethan-nitrile], $CH_3.CN$, melts at —41° C., boils at 81.6°, has a specific gravity of 0.789 (15°), and is a liquid with an agreeable odor. It is usually prepared by distilling acetamide with P_2O_5. Consult the general description of acid nitriles for its methods of formation, its history and its transposition reactions. It may, however, be mentioned here that acetonitrile can be produced from prussic acid and diazomethane (B. **28,** 857).

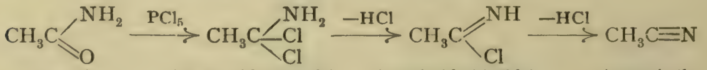
Higher Homologous Nitriles.—Propionitrile, Ethyl Cyanide [Propannitrile], $C_2H_5.CN$, boils at 98°. Its specific gravity equals 0.801 (0°).

n-Butyronitrile boils at 118.5°, and has the odor of bitter-almond oil. **Isobutyronitrile** boils at 107°. **n-Valeronitrile** boils at 140.4°; **isopropylacetonitrile** boils at 129°; **methyl-ethylacetonitrile** boils at 125°; **trimethylacetonitrile** melts at 15–16° and boils at 105–106°. **Isobutylacetonitrile** boils at 154°; **diethylacetonitrile** boils at 144–146°; **dimethyl-ethylacetonitrile** boils at 128–130°; **n-œnanthylnitrile** boils at 175–178°; **n-caprilonitrile** boils at 198–200°; **pelargonitrile** boils at 214–216°; **methyl-n-hexylacetonitrile** boils at 206°; **lauronitrile** boils at 198° (100 mm.); **tridecylonitrile** boils at 275°; **myristonitrile** melts at 19° and boils at 226.5° (100 mm.); **palmitonitrile** melts at 29° and boils at 251.5° (100 mm.); **cetyl cyanide** melts at 53°; **stearonitrile** melts at 41° and boils at 274.5° (100 mm.).

Several classes of compounds bear genetic relations to the acid amides and nitriles, but these will be considered after the nitriles.

9. AMID-CHLORIDES and 10. IMID-CHLORIDES (Wallach, A. 184, 1).

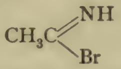
The amid-chlorides are the first unstable products arising in the action of PCl_5 upon acid amides. They part with hydrochloric acid and become *imid-chlorides,* which by a further separation of hydrochloric acid yield nitriles:



$$CH_3C\begin{cases}NH_2\\O\end{cases} \xrightarrow{PCl_5} CH_3C\begin{cases}NH_2\\Cl\\Cl\end{cases} \xrightarrow{-HCl} CH_3C\begin{cases}NH\\Cl\end{cases} \xrightarrow{-HCl} CH_3C{\equiv}N$$

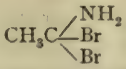
Acetamide (Acetamid-chloride) (Acetimid-chloride) Acetonitrile.

The addition of HCl to the nitriles produces the imid-chlorides. Hydrogen bromide and hydrogen iodide add themselves more readily than hydrogen chloride to nitriles (B. **25**, 2541):



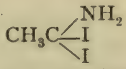
$\mathrm{CH_3C}\begin{matrix}\mathrm{=NH}\\ \mathrm{-Br}\end{matrix}$

Acetimid-bromide



$\mathrm{CH_3C}\begin{matrix}\mathrm{-NH_2}\\ \mathrm{-Br}\\ \mathrm{-Br}\end{matrix}$

Acetamid-bromide



$\mathrm{CH_3C}\begin{matrix}\mathrm{-NH_2}\\ \mathrm{-I}\\ \mathrm{-I}\end{matrix}$

Acetamid-iodide.

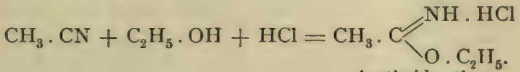
If a hydrogen atom of the amid-group be replaced by an alcohol radical, the imid-chlorides will be more stable. On heating, however, they lose hydrochloric acid in part and pass into chlorinated bases.

(1) Water changes the imid-chlorides back into *acid amides*. The chlorine atom of these bodies is as reactive as the chlorine atom of the acid chlorides. (2) Ammonia and the primary and secondary amines change the imid-chlorides to *amidines* (see below). (3) Hydrogen sulphide converts the imid-chlorides into thiamides.

11. IMIDO-ETHERS* (Pinner, B. 16, 353, 1654; 17, 184, 2002).

The imido-ethers may be regarded as the esters of the imido-acids, $\mathrm{R'.C}\begin{matrix}\mathrm{=NH}\\ \mathrm{-OH}\end{matrix}$, a formula which has, in recent times, been proposed for the acid amides (p. 262); compare also the thiamides.

The hydrochlorides of the **Imido-ethers** are produced by the action of HCl upon an ethereal mixture of a nitrile with an alcohol (in molecular quantities):



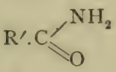
$$\mathrm{CH_3.CN + C_2H_5.OH + HCl = CH_3.C}\begin{matrix}\mathrm{=NH.HCl}\\ \mathrm{-O.C_2H_5.}\end{matrix}$$

Acetimido-ether.

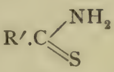
Formimido-ether (p. 232), **Acetimido-ethyl Ether**, when liberated from its HCl-salt by means of NaOH, is a peculiar-smelling liquid. Ammonia and the amines convert the imido-ethers into *amidines*.

12. THIAMIDES.

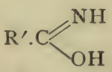
As in the case of the acid amides (p. 262), so here with the thiamides two formulas are possible:



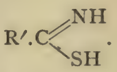
$\mathrm{R'.C}\begin{matrix}\mathrm{-NH_2}\\ \mathrm{=O}\end{matrix}$



$\mathrm{R'.C}\begin{matrix}\mathrm{-NH_2}\\ \mathrm{=S}\end{matrix}$ and



$\mathrm{R'.C}\begin{matrix}\mathrm{=NH}\\ \mathrm{-OH}\end{matrix}$



$\mathrm{R'.C}\begin{matrix}\mathrm{=NH}\\ \mathrm{-SH}\end{matrix}$.

The thiamides are formed (1) by letting phosphorus sulphide act upon the acid amides (p. 262); (2) by the addition of H_2S to the *nitriles*:

$$\underset{\text{Acetonitrile}}{\mathrm{CH_3.CN}} + \mathrm{H_2S} = \underset{\text{Thiacetamide.}}{\mathrm{CH_3.CS.NH_2}}.$$

(1) The thiamides are readily broken up into fatty acids, SH_2, NH_3 and amines.

(2) They yield *thiazole* derivatives with chloracetic ester, chloracetone, and similar bodies.

(3) Ammonia converts them into amidines.

(4) The action of hydroxylamine results in the production of oxamidines.

Thiacetamide melts at 108° (A. **192**, 46; B. **11**, 340). *Thiopropionamide* melts at 42–43° (A. **259**, 229).

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* The Imido-ethers and their Derivatives, A. Pinner, 1892.

13. AMIDINES, $R.C\begin{smallmatrix}\diagup NH\\ \diagdown NH_2\end{smallmatrix}$ (A. 184, 121; 192, 46).

The amidines, containing an amid- and imid-group, whose hydrogen atoms are replaceable by alkyls, may be considered derivatives of the acid amides, in which the carbonyl oxygen is replaced by the imid-group:

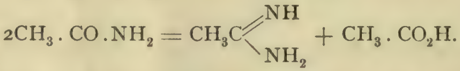
$CH_3.CONH_2$	$CH_3C(NH)NH_2$.
Acetamide	Acetamidine.

They are produced:

(1) From the imid-chlorides and thiamides, by the action of ammonia or amines.

(2) From the nitriles by heating them with ammonium chloride.

(3) From the amides of the acids when treated with HCl (B. **15**, 208):

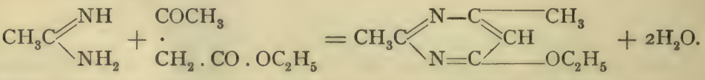


$$2CH_3.CO.NH_2 = CH_3C\begin{smallmatrix}\diagup NH\\ \diagdown NH_2\end{smallmatrix} + CH_3.CO_2H.$$

(4) From the imido-ethers (p. 269) when acted upon with ammonia and amines (B. **16**, 1647; **17**, 179).

The amidines are mono-acid bases. In a free condition they are quite unstable. The action of various reagents on them induces water absorption, the imid-group splits off, and acids or amides of the acids are regenerated.

β-Ketonic esters convert them into *pyrimidines*, *e. g.*, acetamidine hydrochloride and aceto-acetic ester yield *dimethyl-ethoxypyrimidine*, melting at **192°** (compare polym. acetonitrile, p. 268):



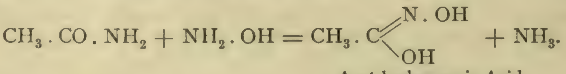
$$CH_3C\begin{smallmatrix}\diagup NH\\ \diagdown NH_2\end{smallmatrix} + \begin{matrix}COCH_3\\ \cdot\\ CH_2.CO.OC_2H_5\end{matrix} = CH_3C\begin{smallmatrix}\diagup N-C & CH_3\\ & CH\\ \diagdown N=C & OC_2H_5\end{smallmatrix} + 2H_2O.$$

Formamidine (p. 232).

Acetamidine (**Acediamine**), *Ethenylamidine*, $CH_3C(NH_2)NH$. Its hydrochloric acid salt melts at 163°. The acetamidine, separated by alkalies, reacts strongly alkaline and readily breaks up into NH_3 and acetic acid.

14. HYDROXAMIC ACIDS, $R.C\begin{smallmatrix}\diagup N.OH\\ \diagdown OH\end{smallmatrix}$.

These are produced when free hydroxylamine, or its hydrochloride, is allowed to act upon acid amides, esters and acid chlorides. They contain the isonitroso group in the place of the carbonyl oxygen (B. **22**, 2854):



$$CH_3.CO.NH_2 + NH_2.OH = CH_3.C\begin{smallmatrix}\diagup N.OH\\ \diagdown OH\end{smallmatrix} + NH_3.$$

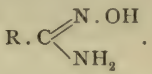
Acet-hydroxamic Acid.

They are crystalline compounds, acid in character, and form an insoluble copper salt in ammoniacal copper solutions. Ferric chloride imparts a cherry-red color to both their acid and neutral solutions.

Acet-hydroxamic Acid, $CH_3.C(N.OH).OH$, with $\frac{1}{2}H_2O$, melts at 59°. It dissolves very easily in water and alcohol, but not in ether.

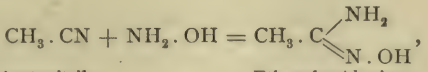
15. NITROLIC ACIDS, $R.C\begin{smallmatrix}\diagup N.OH\\ \diagdown NO_2\end{smallmatrix}$ (p. 157).

As these bodies are genetically related to the mononitro-paraffins, they have already been discussed immediately after them.



16. AMIDOXIMES or OXAMIDINES, $R.C\begin{cases}N.OH\\NH_2\end{cases}$.

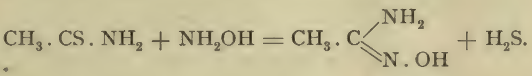
These compounds may be regarded as amidines, in which an H atom of the amid- or imid-group has been replaced by hydroxyl. They are formed: by the action of hydroxylamine on the amidines (p. 270); by the addition of hydroxylamine to the nitriles (B. **17**, 2746):



$$CH_3.CN + NH_2.OH = CH_3.C\begin{cases}NH_2\\N.OH\end{cases},$$

Acetonitrile — Ethenylamidoxime.

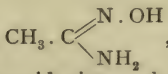
and by the action of hydroxylamine upon thiamides (B. **19**, 1668):



$$CH_3.CS.NH_2 + NH_2OH = CH_3.C\begin{cases}NH_2\\N.OH\end{cases} + H_2S.$$

The amidoximes are crystalline, very unstable compounds, which readily break down into hydroxylamine, and the acid amides or acids.

Methenyl-amidoxime, Formamidoxime or Isuretine (p. 233).



Ethenyl-amidoxime, $CH_3.C\begin{cases}N.OH\\NH_2\end{cases}$, melts at 135°. **Hexenyl-amidoxime** melts at 48°. **Heptenyl-amidoxime** melts at 48–49° (B. **25**, R. 637). **Laurin-amidoxime** melts at 92–92.5°. **Myristin-amidoxime** melts at 97°. **Palmitin-amidoxime** melts at 101.5–102°. **Stearin-amidoxime** melts at 106–106.5° (B. **26**, 2844).

When the aromatic derivatives are discussed we shall again meet with bodies belonging to the classes which have just been considered, viz., the *imid-chlorides*, *imido-ethers*, *thiamides*, *amidines*, *hydroxamic acids* and *amidoximes*. The aromatic primary amines, *e. g.*, *aniline* and *toluidine*, are not only prepared technically on a large scale, but they are more readily accessible than the primary, aliphatic bases, and are more easily handled because of their slighter volatility. Beginning with them, phenylated, etc., derivatives of the aliphatic imid-chlorides have been prepared. On the other hand, benzoic acid and its homologues are excellent material for the study of the carboxyl derivatives of a monocarboxylic acid. This acid imparts the power of crystallization to many of its compounds, and that, again, renders easy the work with them. Hence, the corresponding aromatic derivatives supplement the aliphatic imid-chlorides, etc.

HALOGEN SUBSTITUTION PRODUCTS OF THE FATTY ACIDS.

The reactions leading to the substituted fatty acids are partly the same as those employed in the formation of the halogen substitution products of the paraffins.

(1) *Direct substitution of the hydrogen* of the hydrocarbon residue, joined to carboxyl, by halogens.

(*a*) Chlorine in sunlight, or with the addition of water and iodine, or sulphur (B. **25**, R. 797), or phosphorus (B. **24**, 2209).

(*b*) Bromine in sunlight, or with the addition of water in a closed tube at a more elevated temperature, or with the addition of sulphur (B. **25**, 3311), or phosphorus (B. **24**, 2209).

(*c*) Iodine with iodic acid, or brom-fatty acids with potassium iodide.

The *acid chlorides*, *bromides*, or *acid anhydrides* are more readily substituted than the free acids. When chlorine or bromine, in the presence of phosphorus, acts upon the fatty acids (method of Hell-Volhard), acid chlorides and bromides result; these then are subjected to substitution. The final products are halogen-acid chlorides or halogen-acid bromides:

$$3CH_3.CO_2H + P + 11Br = 3CH_2Br.COBr + HPO_3 + 5HBr.$$

However, substitution only takes place in a mono-alkyl or dialkyl-acetic acid at the α-carbon atom. Hence, *trimethylacetic acid* cannot be chlorinated or brominated. Consequently the deportment of a fatty acid towards chlorine or bromine and phosphorus indicates whether or not a trialkyl-acetic acid is present (B. **24**, 2209).

(2) *Addition of Haloid Acids to Unsaturated Monocarboxylic Acids.*—The halogen enters at a point as far as possible from the carboxyl group, *e. g.*:

$$\underset{\text{Acrylic Acid}}{CH_2:CH.CO_2H}\left\{\begin{array}{l} \xrightarrow{HCl} CH_2Cl.CH_2.CO_2H \\ \xrightarrow{HBr} CH_2Br.CH_2.CO_2H \\ \xrightarrow{HI} CH_2I.CH_2.CO_2H \end{array}\right.\quad\left.\begin{array}{l}\beta\text{-Chlor-}\\ \beta\text{-Brom-}\\ \beta\text{-Iodo-}\end{array}\right\}\text{propionic acid.}$$

(3) *Addition of Halogens to Unsaturated Monocarboxylic Acids.*—Whenever possible the chlorine is allowed to act in a CCl_4 solution. Bromine often adds itself without the help of a solvent, and also in the presence of water, CS_2, glacial acetic acid and chloroform.

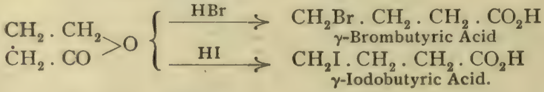
(4) Action of the haloid acids (*a*) upon oxymonocarboxylic acids:

Hydracrylic Acid: $CH_2(OH)CH_2CO_2H \xrightarrow[120^\circ]{HCl} CH_2Cl.CH_2.CO_2H$ β-Chlorpropionic Acid

Lactic Acid: $CH_3CH(OH)CO_2H \xrightarrow{HBr} CH_3CHBrCO_2H$ α-Brompropionic Acid

Glyceric Acid: $CH_2(OH)CH(OH)CO_2H \xrightarrow{HI} CH_2I.CH_2.CO_2H$ β-Iodopropionic Acid.

(4*b*) Upon lactones, cyclic anhydrides of γ- or δ-oxyacids:



$$\begin{matrix}CH_2.CH_2\\ \dot{C}H_2.CO\end{matrix}\!>\!O\left\{\begin{array}{ll}\xrightarrow{\quad HBr\quad} & \underset{\gamma\text{-Brombutyric Acid}}{CH_2Br.CH_2.CH_2.CO_2H}\\ \xrightarrow{\quad HI\quad} & \underset{\gamma\text{-Iodobutyric Acid.}}{CH_2I.CH_2.CH_2.CO_2H}\end{array}\right.$$

(5) Action of the phosphorus haloids, particularly PCl_5, upon oxymonocarboxylic acids. The product is the chloride of a chlorinated acid, which water transforms into the acid:

$$\underset{\text{Lactic Acid}}{CH_3.CHOH.COOH} + 2PCl_5 = \underset{\alpha\text{-Chlorpropionyl Chloride.}}{CH_3.CHCl.COCl} + 2POCl_3 + 2HCl.$$

Furthermore, halogen fatty acids are obtained like the parent acids (6) by the oxidation of *chlorinated alcohols* or *aldehydes* (p. 197) with nitric acid, chromic acid, potassium permanganate or potassium chlorate (B. **18**, 3336):

αβ-Dichlorhydrin: $CH_2Cl.CHCl.CH_2OH \xrightarrow{2O} CH_2Cl.CHCl.CO_2H$ αβ-Dichlorpropionic Acid

Chloral: $CCl_3.CHO \xrightarrow{\qquad O \qquad} CCl_3.COOH$ Trichloracetic Acid.

(7) By the action of halogen hydrides upon diazo-fatty acid esters (see glyoxylic acid):

$$CHN_2 . CO_2 . C_2H_5 + HCl = CH_2Cl . CO_2C_2H_5 + N_2.$$

(8) When the halogens act upon diazo-fatty acid esters:

$$CHN_2CO_2C_2H_5 + I_2 = CHI_2CO_2C_2H_5 + N_2.$$

Isomerism and Nomenclature.—Structurally, isomeric halogen substitution products of the fatty acids are first possible with propionic acid. To indicate the position of the halogen atoms, the carbon atom to which the carboxyl group is attached is marked α, while the other carbon atoms are successively called β, γ, δ, ϵ, etc. The two monochlorpropionic acids are distinguished as α- and β-chlorpropionic acids, while the three isomeric dichlorpropionic acids are the $\alpha\alpha$-, $\beta\beta$- and $\alpha\beta$ dichlorpropionic acid, etc.

Deportment.—The introduction of substituting halogen atoms increases the acid character of the fatty acids. The halogen fatty acids, like the parent acids, yield, by analogous treatment, *esters*, *chlorides*, *anhydrides*, *amides*, *nitriles*, etc.

Transpositions.—(1) Nascent hydrogen causes the halogen substitution products of the fatty acids to revert to the parent acids—*retrogressive substitution.*

The transpositions of the monohaloid fatty acids, which bear the same relation to the *alcohol acids* or *oxyacids* as the alkylogens sustain to the alcohols, are especially important. In both classes the halogen atoms enter the reaction under similar conditions.

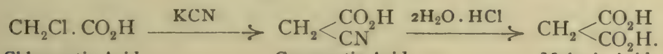
(2) Boiling water, caustic alkali, or an alkaline carbonate solution generally brings about an exchange of hydroxyl for the halogen atom.

However, in monohalogen products, the position of the halogen atom, with reference to carboxyl, will materially affect the course of the reaction: α-halogen acids yield α-oxyacids, β-haloid acids split off the haloid acid and become unsaturated acids; γ-halogen acids, on the contrary, yield γ-oxyacids, which readily yield *lactones* (B. **219**, 322):

$$CH_2Cl . COOH \xrightarrow{H_2O} CH_2(OH)CO_2H$$
$$CH_2Cl . CH_2 . COOH \xrightarrow{H_2O} CH_2 = CH . CO_2H$$
$$CH_2Cl . CH_2 . CH_2 . COOH \xrightarrow{H_2O} CH_2\overline{O . CH_2 . CH_2C}O.$$

(3) Ammonia converts the halogen fatty acids into amido-acids.

Nucleus-synthetic Reactions.—(4) Potassium cyanide produces cyanfatty acids—*half-nitrile fatty-acids*, which hydrochloric acid changes to dibasic acids. They will be considered after the latter:



$$CH_2Cl . CO_2H \xrightarrow{KCN} CH_2{<}\begin{matrix}CO_2H\\CN\end{matrix} \xrightarrow{2H_2O . HCl} CH_2{<}\begin{matrix}CO_2H\\CO_2H.\end{matrix}$$

Chloracetic Acid — Cyanacetic Acid — Malonic Acid.

The monohalogen acids furnish a means of building up the dicarbonic acids from the monocarboxylic acids.

(5) *Dicarboxylic acids* have been obtained from monohalogen carboxylic acids by means of metals (Ag):

$$2CH_2ICH_2CO_2H + 2Ag = \underset{\text{Adipic Acid.}}{\begin{array}{l}CH_2 \,.\, CH_2 \,.\, CO_2H \\ \dot{C}H_2 \,.\, CH_2 \,.\, CO_2H\end{array}} + 2AgI.$$

(6) and (7) The esters of the mono-haloid fatty acids have been applied in the circle of the aceto-acetic ester and malonic ester syntheses, and as results we have β-ketone-dicarboxylic acids, β-ketone-tricarboxylic acids, and tricarboxylic and tetracarboxylic acids.

Substitution Products of Acetic Acid.

Chlorine Substitution Products.—The relations of the three chloracetic acids to the oxygen derivatives, whose anhydrides they may be considered, are evident in the following tabulation (compare pp. 125, 199):

Monochloracetic Acid, $CH_2Cl \,.\, CO_2H$, corresponds to Glycollic Acid, $CH_2OH \,.\, CO_2H$
Dichloracetic Acid, $CHCl_2 \,.\, CO_2H$, corresponds to Glyoxylic Acid, $CHO \,.\, CO_2H$
Trichloracetic Acid, $CCl_3 \,.\, CO_2H$, corresponds to Oxalic Acid, $CO_2H \,.\, CO_2H$.

Monochloracetic Acid, $CH_2Cl \,.\, CO_2H$, melts at 62° and boils at 185–187°. After fusion it solidifies to an unstable modification, melting at 52°. This slowly reverts spontaneously to the ordinary acid (B. **26**, R. 381). Its sodium and silver salts, on the application of heat, yield *polyglycolide*.

When monochloracetic acid is heated with alkalies or water, the chlorine is replaced by the hydroxyl group, and we get oxyacetic acid or glycollic acid ($C_2H_3(OH)O_2$). Amido-acetic acid, $CH_2(NH_2) \,.\, CO_2H$, or glycocoll, results when the monochloracid is digested with ammonia.

The *ethyl ester* boils at 143.5°.

The *chloride* boils at 106°; the *bromide*, at 127°; the *anhydride* melts at 46° and boils at 110° (11 mm.) (B. **27**, 2949); the *amide* melts at 116° and boils at 224–225°; the *nitrile* boils at 124°.

Dichloracetic Acid, $CHCl_2 \,.\, CO_2H$, is produced when chloral is heated with CNK or potassium ferrocyanide and some water. If alcohol replace the water, dichloracetic esters are formed. The prussic acid in the presence of chloral effects a decomposition of water into its components (B. **10**, 2124):

$$CCl_3 \,.\, CHO + H_2O + CNK = CHCl_2 \,.\, CO_2H + KCl + CNH.$$

It boils at from 190°–191°. When its silver salt is boiled with a little water, *glyoxylic acid* (see this) is produced.

Methyl ester boils at 142°–144°.

The *ethyl ester* boils at 158°. The *anhydride* boils at 214°–216°, without decomposition; the *amide* melts at 98° and boils at 234°; the *nitrile* boils at 113°.

Trichloracetic Acid, $CCl_3 \,.\, CO_2H$, the officinal *Acidum trichloraceticum*, was first prepared by Dumas (1839) when he allowed chlorine to act in the sunlight upon acetic acid (A. **32**, 101). Without essentially changing the chemical character, three hydrogen atoms of the acetic acid were replaced by chlorine—a fact upon which Dumas then erected the *type theory* (p. 35). Kolbe (1845) made the acid by the oxidation of chloral with concentrated nitric acid (A. **54**, 183), and demonstrated how it could be prepared synthetically from its elements:

$$C + 2S \longrightarrow CS_2 \xrightarrow{Cl_2} CCl_4 \xrightarrow{\text{Heat}} \begin{array}{c}CCl_2 \\ \| \\ CCl_2\end{array} \xrightarrow[\text{Sunlight}]{Cl_2,\ 2H_2O} \begin{array}{c}COOH \\ | \\ CCl_3\end{array}.$$

The carbon disulphide resulting from carbon and sulphur is converted by the chlorine into carbon tetrachloride, which on the application of heat becomes perchlorethylene, $CCl_2 = CCl_2$ (p. 105), and it, in turn, by the action of chlorine and water, aided by sunlight, yields trichloracetic acid. This was the first synthesis of acetic acid, for Melsens had previously shown that potassium amalgam in aqueous solution reduced trichloracetic acid to acetic acid (p. 244).

When digested with ammonia or alkalies, the acid breaks down into chloroform (p. 234) and a carbonate.

The *methyl ester* boils at 152.5°, and the *ethyl ester* at 164°. They are obtained from the acid and alcohols (B. **29**, 2210). *Trichloracetyl chloride*, Perchloracetaldehyde, boiling at 118°, is formed when ozonized air acts upon perchlorethylene (B. **27**, R. 509); compare synthesis of trichloracetic acid from CS_2. The *bromide* boils at 143°; the *anhydride* at 224°; the *amide* melts at 141° and boils at 239°; the *nitrile* boils at 83°. *Perchloracetic methyl ester*, $CCl_3 . CO_2CCl_3$, melts at 34° and boils at 192° (A. **273**, 61).

Bromacetic Acids.—Monobromacetic Acid, $CH_2Br . CO_2H$, melts at 50–51° and boils at 208°; the *ethyl ester* boils at 159°; the *chloride* boils at 134°; the *bromide*, $CH_2Br . COBr$, boils at 150° (pp. 105, 258); the *anhydride* boils at 245°; the *amide* melts at 91°, and the *nitrile* boils at 148–150°.

Dibromacetic Acid, $C_2H_2Br_2O_2$, melts at 54–56°, and boils at from 232–235°. The *ethyl ester* boils at 192°; the *bromide*, $CHBr_2 . COBr$ (pp. 105, 258), boils at 194°, and the *amide* melts at 156°.

Tribromacetic Acid, $C_2HBr_3O_2$, melts at 135°, and boils at 245°, with decomposition. Its *ethyl ester* boils at 225°; the *bromide* at 220°–225°; the *amide* melts at 120–121°; the *nitrile* boils at 170°. It is a dark red liquid, which HCl changes to the polymeric trinitrile, melting at 129° (B. **27**, R. 730).

Iodoacetic Acids.—Moniodoacetic Acid, $C_2H_3IO_2$, melts at 82°.

Di-iodoacetic Acid, $CHI_2 . CO_2H$, melts at 110°.

Tri-iodoacetic Acid melts at 150°. The last two compounds have been obtained from malonic acid and iodic acid (B. **26**, R. 597). Compare iodoform, page 235.

Substitution Products of Propionic Acid.

The α-monohaloid propionic acids contain an asymmetric carbon atom; hence their esters are known, for example, in an active form. They are prepared according to the methods 4*a* and 5 (p. 272). The β-monohalogen acids are derived from acrylic acid by method 3 (p. 272), and β-iodopropionic acid from glyceric acid by method 4*a*.

α-**Chlorpropionic Acid**, $CH_3 . CHCl . CO_2H$, boils at 186°. Its *ethyl ester* boils at 146°; its *chloride* at 109–110°; its *amide* at 80°; its *nitrile* at 121–122°. α-**Brompropionic Acid** melts at 24.5° and boils at 205°. Its *ethyl ester* boils at 162°; its *bromide* at 153° (A. **280**, 247); its *anhydride* at 120° (5 mm.) (B. **27**, 2949). α-**Iodopropionic Acid** is a thick oil. Dextrorotatory α-**Chlor-** and α-**Brompropionic Esters** have been prepared from sarcolactic acid (B. **28**, 1293).

β-**Chlorpropionic Acid**, $CH_2Cl . CH_2 . CO_2H$, melts at 41.5° and boils at 203–204°. Its *methyl ester* boils at 156°; its *ethyl ester* boils at 162°; its *chloride* at 143–145°. β-**Brompropionic Acid** melts at 61.5°; its *ethyl ester* boils at 69–70° (10 mm.); its *bromide* boils at 154–155°. β-**Iodopropionic Acid** melts at 82°; the *methyl ester* boils at 188°; the *ethyl ester* at 202°; and the *amide* melts at 100° (B. **21**, 24, 97).

Dihalogen Propionic Acids.—$\alpha\alpha$-Acids, from the chlorination and bromination of propionic acid (B. 18, 235); $\alpha\beta$-acids, by the addition of chlorine and bromine to acrylic acid, by the addition of a halogen hydride to α-halogen acrylic acids, and by the oxidation of the corresponding alcohols (p. 272); $\beta\beta$-acids, by the addition of a halogen hydride to β-halogen acrylic acids.

$\alpha\alpha$-**Dichlorpropionic Acid**, $CH_3 . CCl_2 . CO_2H$, boils at 185°–190°. The *ethyl ester* boils at 156°–157°; its *chloride*, from pyroracemic acid and PCl_5, boils at 105°–115°, and the *amide* melts at 116° (B. **11**, 388). The *nitrile* boils at 105° (B. **9**, 1593).

The silver salt changes to $CH_3 . CO . CO_2H$ (pyroracemic acid), and $\alpha\alpha$-dichlorpropionic acid (see B. **18**, 1227).

$\alpha\alpha$-**Dibrompropionic Acid** melts at 61° and boils at 220°. The *ethyl ester* boils at 190°.

$\alpha\beta$-**Dichlorpropionic Acid**, $CH_2Cl . CHCl . CO_2H$, melts at 50° and boils at 210°. The *ethyl ester* boils at 184°.

$\alpha\beta$-**Dibrompropionic Acid** is capable of existing in two allotropic modifications, which can be readily converted one into the other. The one form melts at 51°, the other, more stable, at 64°. The acid boils at 227°, with partial decomposition. The *ethyl ester* boils at 211°–214°.

$\beta\beta$-**Dibrompropionic Acid,** from β-bromacrylic acid and HBr, melts at 71° (B. 27, R. 257).

Substitution Products of the Butyric Acids.

α-**Chlor-n-butyric Acid,** $CH_3 . CH_2 . CHCl . CO_2H$, is a thick liquid. Its *ethyl ester* boils at 156–160°. Its *chloride*, boiling at 129–132°, is obtained from butyryl chloride (A. **153**, 241).

α-**Brombutyric Acid,** from butyric acid, boils at 215°.

β-**Chlor-n-butyric Acid** is obtained from allyl cyanide.

β-**Brom-n-butyric Acid** and β-**Iodo-n-butyric Acid** (melting at 110°) (B. **22**, R. 741) have been obtained from crotonic acid.

γ-**Chlor-n-butyric Acid,** $CH_2Cl . CH_2 . CH_2 . CO_2H$, melts at 10°. **Trimethylene Chlorobromide,** $CH_2Cl . CH_2 . CH_2Br$, and KCN, yield the γ-chlorbutyric nitrile, boiling at 195–197° (B. **23**, 1771). The acid is obtained from this, and when distilled at 200° it yields HCl and butyro-lactone (see this).

γ-**Brom-** and γ-**Iodobutyric** acids result from butyro-lactone (see this) by the action of HBr and HI; the first melts at 33°, the second at 41° (B. **19**, R. 165).

$\alpha\beta$-**Dichlorbutyric Acid,** $CH_3 . CHCl . CHCl . CO_2H$, melts at 63°. $\alpha\beta$-**Dibrombutyric Acid** melts at 85°. Both are obtained from crotonic acid.

$\alpha\alpha\beta$-**Trichlorbutyric Acid,** $C_4H_5Cl_3O_2$, appears in the oxidation of trichlorbutyraldehyde and by the action of chlorine upon chlorcrotonic acids (B. **28**, 2661).

$\alpha\alpha\beta$-**Tribrombutyric Acid** melts at 105°. The solutions of the sodium salts of both acids break down when warmed into CO_2, sodium halide, and $\alpha\alpha$-dichlor- and $\alpha\alpha$-dibrompropylene (B. **28**, 2663).

α-**Bromisobutyric Acid,** $(CH_3)_2 . CBr . CO_2H$, melts at 48° and boils at 198°–200°. Its anhydride melts at 63° (B. **27**, 2951).

Halogen Substitution Products of Higher Fatty Acids.

α-Monobrom-acids of some of the higher fatty acids have been prepared by direct bromination, or by the action of bromine in the presence of phosphorus (B. **25**, 486). Furthermore, such derivatives arise from the addition of halogen hydrides and halogens to unsaturated acids.

The dibrom-addition-products of the unsaturated acids have been exhaustively studied. Water almost invariably sets the COOH free from the $\alpha\beta$-dibromides with the formation of brominated hydrocarbons, etc., whereas carbon is never split off from the $\beta\gamma$- and $\gamma\delta$- derivatives, but the first products are brominated lactones, from which oxylactones and γ-ketonic acids are simultaneously obtained (A. **268**, 55).

B. OLEIC ACIDS, OLEFINE MONOCARBOXYLIC ACIDS,

$C_nH_{2n-1}CO_2H$.

The acids of this series, bearing the name *Oleic Acids*, because oleic acid belongs to them, differ from the fatty acids by containing two atoms of hydrogen less than the latter. They also bear the same relation to them that the alcohols of the allyl series do to the normal alcohols. We can consider them derivatives of the alkylens, C_nH_{2n}, produced by the replacement of one atom of hydrogen by the carboxyl group.

Some of the methods employed for the preparation of the unsaturated acids are similar to those used with the fatty acids. Others correspond to the methods used with the olefines, and others, again, are peculiar to this class of bodies.

From compounds containing a like *carbon content:*

(1) Like the fatty acids, they are produced by the oxidation of their corresponding alcohols and aldehydes; thus, allyl alcohol and its aldehyde afford acrylic acid:

$$\underset{\text{Allyl Alcohol}}{CH_2:CH.CH_2.OH} \longrightarrow \underset{\text{Acroleïn}}{CH_2:CH.CHO} \longrightarrow \underset{\text{Acrylic Acid.}}{CH_2:CH.CO_2H.}$$

(2) The action of alcoholic potash (p. 272) upon the monohalogen derivatives of the fatty acids:

$$\underset{\alpha\text{-Chlorbutyric Acid}}{CH_3.CH_2.CHCl.CO_2H} \text{ and } \underset{\beta\text{-Chlorbutyric Acid}}{CH_3.CHCl.CH_2.CO_2H} \text{ yield } \underset{\text{Crotonic Acid.}}{CH_3.CH:CH.CO_2H}$$

The β-derivatives are especially reactive, sometimes parting with halogen hydrides on boiling with water (p. 272), whereas the γ-halogen acids yield oxy-acids and lactones. (3) Similarly, the $\alpha\beta$-derivatives of the acids (p. 274) readily lose two halogen atoms, (*a*) either by the action of nascent hydrogen—

$$\underset{\alpha\beta\text{-Dibrompropionic Acid}}{CH_2Br.CHBr.CO_2H} + 2H = \underset{\text{Acrylic Acid.}}{CH_2:CH.CO_2H} + 2HBr,$$

or (*b*) even more readily when heated with a solution of potassium iodide, in which instance the primary di-iodo-compounds part with iodine (p. 131):

$$CH_2I.CHI.CO_2H = CH_2:CH.CO_2H + I_2.$$

(4) The removal of water (in the same manner in which the alkylens C_nH_{2n} are formed from the alcohols) from the oxy-fatty acids (the acids belonging to the lactic series):

$$\underset{\alpha\text{-Oxypropionic Acid}}{CH_3.CH(OH).CO_2H} \text{ and } \underset{\beta\text{-Oxypropionic Acid}}{CH_2(OH).CH_2.CO_2H} \text{ yield } \underset{\text{Acrylic Acid.}}{CH_2:CH.CO_2H.}$$

Here again the β-derivatives are most inclined to alteration, losing water when heated. The removal of water from α-derivatives is best accomplished by acting on the esters with PCl_3. The esters of the unsaturated acids are formed first, and can be saponified by means of alkalies.

(5) From the amido-fatty acids by the splitting-off of the amido-group after the previous introduction of the methyl group.

(6) By the addition of hydrogen to acetylene carbonic acids:

$$\text{Tetrolic Acid, } CH_3.C \vdots C.CO_2H + 2H = CH_3.CH:CH.CO_2H, \text{ Crotonic Acid.}$$

Nucleus-synthetic Methods.—(7) Some may be prepared synthetically from the halogen derivatives, $C_nH_{2n-1}X$, aided by the cyanides (see p. 240); thus allyl iodide yields allyl cyanide and crotonic acid, and the point of double union is changed:

$$CH_2 = CHCH_2I \longrightarrow CH_3CH = CHCN \longrightarrow CH_3CH = CHCO_2H.$$

The replacement of the halogen by CN in the compounds $C_nH_{2n+1}X$ is conditioned by the structure of the latter. Although allyl iodide, $CH_2:CH.CH_2I$, yields a cyanide, ethylene chloride, $CH_2:CHCl$, and β-chlorpropylene, $CH_3.CCl:CH_2$, are not capable of this reaction.

(8) Some acids have been synthetically prepared by Perkin's reaction. This is readily executed with benzene derivatives. It proceeds with difficulty in the fatty

series. It consists in letting the aldehydes act upon a mixture of acetic anhydride and sodium acetate (compare Cinnamic Acid):

$$\underset{\text{Œnanthol}}{C_6H_{13}CHO} + CH_3 . CO_2Na = \underset{\text{Nonylenic Acid.}}{C_6H_{13} . CH = CH . CO_2Na} + H_2O.$$

β-Dimethylacrylic acid is obtained from acetone, malonic acid and acetic anhydride (B. **27**, 1574).

Pyroracemic acid acts analogously with sodium acetate; carbon dioxide splits off and crotonic acid results (B. **18**, 987).

Methods of formation, dependent upon the breaking-down of long carbon chains:

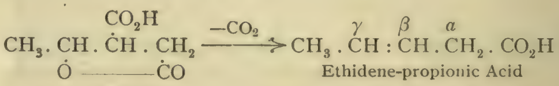
(9) The decomposition of *unsaturated β-ketonic acids*, synthetically prepared by the introduction of unsaturated radicals into aceto-acetic esters. Allyl aceto-acetic ester yields *allyl acetic acid* (p. 284).

(10) Decomposition of *unsaturated malonic acids*, containing the two carboxyl groups attached to the same carbon atom (p. 241):

$$\underset{\text{Ethidene-malonic Acid}}{CH_3 . CH : C(CO_2H)_2} = \underset{\text{Crotonic Acid.}}{CH_3 . CH : CH . CO_2H} + CO_2.$$

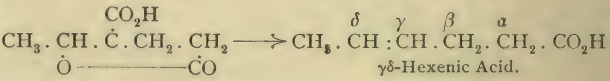
(11) Unsaturated $\beta\gamma$-acids are prepared by distilling γ-lactone-β-carboxylic acids, alkylized paraconic acids (B. **23**, R. 91). In the same manner $\gamma\delta$-unsaturated acids result from the δ-lactone-γ-carbonic acids (B. **29**, 2367):

Methyl paraconic Acid,



$$\begin{array}{l} \qquad\qquad CO_2H \\ CH_3 . CH . \dot{C}H . CH_2 \xrightarrow{-CO_2} CH_3 . \overset{\gamma}{C}H : \overset{\beta}{C}H . \overset{\alpha}{C}H_2 . CO_2H \\ \qquad \dot{O}\text{————}\dot{C}O \qquad\qquad\qquad \text{Ethidene-propionic Acid} \end{array}$$

δ-Caprolactone-γ-carboxylic Acid,



$$\begin{array}{l} \qquad\qquad CO_2H \\ CH_3 . CH . \dot{C} . CH_2 . CH_2 \longrightarrow CH_8 . \overset{\delta}{C}H : \overset{\gamma}{C}H . \overset{\beta}{C}H_2 . \overset{\alpha}{C}H_2 . CO_2H \\ \qquad \dot{O}\text{——————}\dot{C}O \qquad\qquad\qquad \gamma\delta\text{-Hexenic Acid.} \end{array}$$

Isomerism.—An isomeride of acrylic acid is not known, or possible. The second member of the series has three structurally isomeric, open-carbon chain modifications:

(1) $CH_3 . CH = CH . CO_2H$; (2) $CH_2 = CH . CH_2 . CO_2H$; (3) $CH_2 = C{<}^{CO_2H}_{CH_3}$.

In fact, there are three crotonic acids—the ordinary *solid crotonic acid*, *isocrotonic acid* and *methylacrylic acid*. Formerly, formula 2 was ascribed to isocrotonic acid. There is, however, much favoring the view that both acids—the ordinary solid crotonic acid and isocrotonic acid—have the same formula. Hence it is assumed that *crotonic* and *isocrotonic acids* are merely geometric, stereo- or space-isomerides. Compare crotonic acids, p. 282.

Numerous pairs of isomerides, where differences may be similarly indicated, attach themselves to crotonic and isocrotonic acids—angelic and tiglic acids; oleic and elaïdic acid; erucic and brassidic acids.

The monocarboxylic acids of tri-, tetra-, penta-, and hexamethylene are structurally isomeric with the acids $C_3H_5 . CO_2H$, $C_4H_7CO_2H$,

$C_5H_9CO_2H$, $C_6H_{11}CO_2H$. Further, the *trimethylene carboxylic acid*, $\begin{matrix}CH_2\\CH_2\end{matrix}\!>CH.CO_2H$, is isomeric with the three crotonic acids, and *tetramethylene carboxylic acid*, $CH_2<\begin{matrix}CH_2\\CH_2\end{matrix}>CHCO_2H$, etc., with the acids $C_4H_7CO_2H$. Compare p. 89.

Properties and Transpositions.—Like the saturated acids in their entire character, the unsaturated derivatives are, however, distinguished by their ability to take up additional atoms. They unite the properties of a fatty acid with those of an olefine.

(1) On combining with two hydrogen atoms they become fatty acids.

The lower members, as a general thing, combine readily with the H_2 evolved in the action of zinc upon dilute sulphuric acid; while the higher remain unaffected. Sodium amalgam apparently only reduces those acids in which the carboxyl group is in union with the doubly-linked pair of carbon atoms (B. **22**, R. 376). All may be hydrogenized, however, by heating with hydriodic acid and phosphorus.

(2) They combine with halogen hydrides, forming monohalogen fatty acids. In so doing the halogen atom attaches itself as far as possible from the carboxyl group (p. 274).

(3) They unite with the halogens to form dihalogen fatty acids (p. 274).

All these transformations have already been given as methods of forming fatty acids and their halogen derivatives.

(4) Ammonia converts the olefine carboxylic acids into amido-fatty acids; crotonic acid yields β-amidobutyric acid. Hydrazine and phenylhydrazine deport themselves similarly with the same compounds.

(5) Diazoacetic ester combines with the olefine carboxylic esters to produce pyrazoline carboxylic ester; acrylic ester and diazoacetic ester yield 3.4-pyrazoline carboxylic ester (see this) (Buchner, A. **273**, 222).

(6) The behavior of unsaturated acids toward alkalies is especially noteworthy.

(*a*) When heated to 100°, with KOH or NaOH, they frequently absorb the elements of water and pass into oxy-acids. Thus, from acrylic acid we obtain α-lactic acid ($CH_2:CH.CO_2H + H_2O = CH_3.CH(OH).CO_2H$), and malic from fumaric acid, etc.

(*b*) $\beta\gamma$-Unsaturated acids rearrange themselves to $\alpha\beta$-unsaturated acids (Fittig, A. 283, 47, 269; B. **28**, R. 140) when they are boiled with caustic alkali; the double union is made to take a new position:

$$\underset{\text{Hydrosorbic Acid}}{\overset{\epsilon}{C}H_3.\overset{\delta}{C}H_2.\overset{\gamma}{C}H=\overset{\beta}{C}H.\overset{\alpha}{C}H_2.COOH} \longrightarrow \underset{\text{n-Butylidene Acetic Acid.}}{\overset{\epsilon}{C}H_3.\overset{\delta}{C}H_2.\overset{\gamma}{C}H_2.\overset{\beta}{C}H:\overset{\alpha}{C}H.COOH.}$$

(*c*) When fused with potassium or sodium hydroxide their double union is severed and two monobasic fatty acids result:

$$\underset{\text{Acrylic Acid}}{CH_2:CH.CO_2H} + 2H_2O = \underset{\text{Formic Acid}}{CH_2O_2} + \underset{\text{Acetic Acid}}{CH_3.CO_2H} + H_2$$

$$\underset{\text{Crotonic Acid}}{CH_3CH:CH.CO_2H} + 2H_2O = \underset{\text{Acetic Acid}}{CH_3.CO_2H} + \underset{\text{Acetic Acid.}}{CH_3.CO_2H} + H_2.$$

The decomposition occasioned by fusion with alkali is not a reaction which can be applied in ascertaining constitution, because under the influence of the alkali there may occur a displacement or rearrangement of the double union.

(7) Oxidizing agents like chromic acid, nitric acid and permanganate of potash have the same effect as alkalies. (*a*) The group linked to carboxyl is usually further oxidized, and thus a dibasic acid results.

(*b*) When carefully oxidized with permanganate, the unsaturated acids sustain an alteration similar to that of the olefines; dioxy-acids result (Fittig, B. **21**, 1887).

$$\underset{\alpha\text{-Ethyl Crotonic Acid}}{CH_3.CH : C(C_2H_5)CO_2H} + O + H_2O = \underset{\alpha\text{-Ethyl-}\beta\text{-methyl Glyceric Acid.}}{CH_3CH(OH)\!-\!C(OH)(C_2H_5)CO_2H}$$

(8) $\beta\gamma$-Unsaturated acids when heated with dilute sulphuric acid change to γ-lactones:

$$\underset{\text{Pyroterebic Acid}}{(CH_3)_2C : CH . CH_2CO_2H} \longrightarrow \underset{\text{Isocaprolactone.}}{(CH_3)_2C . CH_2 . CH_2 . COO}$$

1. **Acrylic Acid** [*Propen-Acid*], $CH_2 : CH . CO_2H$, melting at 7° and boiling at 139–140°, is obtained according to the general methods:

(1) From β-chlor-, β-brom-, or β iodo-propionic acid by the action of alcoholic potash or lead oxide.

(2) From $\alpha\beta$-dibrompropionic acid by the action of zinc and sulphuric acid, or potassium iodide.

(3) By heating β-oxypropionic acid (hydracrylic acid).

The best method consists in oxidizing acroleïn with silver oxide, or by the transposition of acroleïn, by successive treatment with hydrochloric and nitric acid, into β-chlorpropionic acid, and the subsequent decomposition of this acid by caustic alkali (B. **26**, R. 777).

Acrylic acid is a liquid with an odor like that of acetic acid. It is miscible with water. If allowed to stand for some time, it is transformed into a solid polymeride. By protracted heating on the water-bath with zinc and sulphuric acid it is converted into *propionic acid.* This change does not occur in the cold. It combines with bromine to form *$\alpha\beta$ dibrompropionic acid*, and with the halogen hydrides to yield *β substitution products* of propionic acid (p. 275). If fused with caustic alkalies, it is broken up into acetic and formic acids.

The *silver salt*, $C_3H_3O_2Ag$, consists of shining needles. The *lead salt*, $(C_3H_3O_2)_2Pb$, crystallizes in long, silky, glistening needles.

The *ethyl ester*, $C_3H_3O_2 . C_2H_5$, obtained from the ester of $\alpha\beta$-dibrompropionic acid by means of zinc and sulphuric acid, is a pungent-smelling liquid boiling at 101–102°. The *methyl ester* boils at 85°, and after some time polymerizes to a solid mass.

Acryl chloride, $CH_2 : CH . CO . Cl$, boils at 75–76°; *acrylic anhydride* $[CH_2 : CH . CO]_2O$, boils at 97° (35 mm.); *acryl amide*, $CH_2 : CH . CONH_2$, melts at 84–85°, and *acryl nitrile*, vinyl cyanide, $CH_2 : CH . CN$, boils at 78° (B. **26**, R. 776).

Substitution Products.—There are two isomeric forms of mono- and di-substituted acrylic acids.

α-**Chloracrylic Acid**, $CH_2 : CCl . CO_2H$, results when $\alpha\beta$- and also $\alpha\alpha$-dichlorpropionic acids are heated with alcoholic potash. It melts at 64–65°. It combines with HCl at 100° to produce $\alpha\beta$-dichlorpropionic acid (B. **10**, 1499; **18**, 244).

β-**Chloracrylic Acid** is produced together with dichloracrylic acid in the reduction of *chloralide* with zinc and hydrochloric acid (A. **203**, 83; **239**, 263), also from *propiolic acid*, $C_3H_2O_2$ (p. 287), by the addition of HCl. It melts at 84° (A. **203**, 83). It unites with HCl to *ββ*-dichlorpropionic acid. The *ethyl ester* boils at 146°.

α-**Bromacrylic Acid** melts at 69–70°.

β-**Bromacrylic Acid** melts at 115–116°.

β **Iodoacrylic Acid**, $C_3H_3IO_2$, is known in two modifications, one melting at 139–140°, the other at 65° (B. **19**, 542).

αβ-**Dichloracrylic Acid** melts at 87°. *ββ*-**Dichloracrylic Acid** melts at 76–77°.

αβ-**Dibromacrylic Acid** and *ββ*-**Dibromacrylic Acid** both melt at 85–86°.

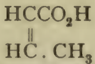
αβ-**Di-iodo-acrylic Acid** melts at 106°; *ββ*-**Di-iodo-acrylic Acid** melts at 133° (B. **18**, 2284).

Trichloracrylic Acid melts at 76°.

Tribromacrylic Acid melts at 117–118°.

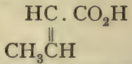
2. Crotonic Acids, $C_3H_5 . CO_2H$.

In the introduction to the olefine carboxylic acids the isomerism of the crotonic acids was made evident, and it was shown that the cause of the difference between crotonic and isocrotonic or quartenylic acid was sought in the different arrangement of the atoms in the molecules of the two acids, in the sense of the following formulas (A. **248**, 281):



$$\begin{array}{c}HCCO_2H\\ \|\\ HC . CH_3\end{array}$$

Crotonic Acid
(Plane Symmetric Config.)



$$\begin{array}{c}HC . CO_2H\\ \|\\ CH_3CH\end{array}$$

Isocrotonic or Quartenylic Acid.
(Axial Symmetric Config.)

The ordinary solid crotonic acid is the *cis*-crotonic acid, because it can be reduced by means of sodium amalgam to tetrolic acid (B. **22**, 1183); and isocrotonic acid would then be the *cis-trans*-crotonic acid (p. 51). (However, the experimental basis for the determination of the so-called configurations are very uncertain; compare B. **25**, R. 855, 856; J. pr. Ch. [2] **46**, 402. Furthermore, the unitary nature of isocrotonic acid has again been thrown in doubt; compare B. **26**, 108; and also A. **268**, 16; **283**, 47; B. **29**, 1639).

The melting and boiling points of both crotonic acids and their monochlor- and dichlor-substitution products are presented below in a tabular form:

(1) **Crotonic Acid**	$\begin{smallmatrix}CH_3\\H\end{smallmatrix}\!>C:C<\!\begin{smallmatrix}CO_2H\\H\end{smallmatrix}$	m. p.	72°;	b. p. 180°.
(1*a*) *α*-**Chlorcrotonic Acid**	$\begin{smallmatrix}CH_3\\H\end{smallmatrix}\!>C:C<\!\begin{smallmatrix}CO_2H\\Cl\end{smallmatrix}$	"	99°;	" 212°.
(1*b*) *β*-**Chlorcrotonic Acid**	$\begin{smallmatrix}CH_3\\Cl\end{smallmatrix}\!>C:C<\!\begin{smallmatrix}CO_2H\\H\end{smallmatrix}$	"	94°;	" 200°.
(1*c*) *α*-**Bromcrotonic Acid**	$\begin{smallmatrix}CH_3\\H\end{smallmatrix}\!>C:C<\!\begin{smallmatrix}CO_2H\\Br\end{smallmatrix}$	"	106.5°.	
(1*a*) *β*-**Bromcrotonic Acid**	$\begin{smallmatrix}CH_3\\Br\end{smallmatrix}\!>C:C<\!\begin{smallmatrix}CO_2H\\H\end{smallmatrix}$	"	95°.	
(2) **Isocrotonic Acid**	$\begin{smallmatrix}H\\CH_3\end{smallmatrix}\!>C:C<\!\begin{smallmatrix}CO_2H\\H\end{smallmatrix}$	liquid		" 75° (23 mm.).
(2*a*) *α*-**Chlorisocrotonic Acid**	$\begin{smallmatrix}H\\CH_3\end{smallmatrix}\!>C:C<\!\begin{smallmatrix}CO_2H\\Cl\end{smallmatrix}$	m. p.	66.5°.	
(2*b*) *β*-**Chlorisocrotonic Acid**	$\begin{smallmatrix}Cl\\CH_3\end{smallmatrix}\!>C:C<\!\begin{smallmatrix}CO_2H\\H\end{smallmatrix}$	"	59°;	" 195°.
(2*c*) *α*-**Bromisocrotonic Acid**	$\begin{smallmatrix}H\\CH_3\end{smallmatrix}\!>C:C<\!\begin{smallmatrix}CO_2H\\Br\end{smallmatrix}$	"	92°.	

1. **Ordinary Crotonic Acid** is obtained:

(1) By the oxidation of crotonaldehyde, $CH_3.CH:CH.COH$ (p. 277).

(2) By the action of alcoholic potash upon α-brombutyric acid and β-iodobutyric acid and

(3) KI upon $\alpha\beta$-dibrombutyric acid.

(4) By the dry distillation of β-oxybutyric acid, $CH_3.CH(OH).CH_2.CO_2H$.

(5) By the action of sodium amalgam on tetrolic acid.

(6) From allyl iodide by means of the cyanide (B. **21**, 494).

(7) The most practicable method of obtaining crotonic acid is to heat malonic acid, $CH_2(CO_2H)_2$, with paraldehyde and acetic anhydride. The ethidene malonic acid first produced decomposes into CO_2 and crotonic acid (p. 278) (A. **218**, 147).

Crotonic acid crystallizes in fine, woolly needles or in large plates. It dissolves in 12 parts water at 20°. The warm aqueous solution will reduce alkaline silver solutions with the formation of a silver mirror. Zinc and sulphuric acid, but not sodium amalgam, convert it into normal butyric acid. It combines with HBr and HI to yield β-brom- and β-iodobutyric acid, and with chlorine and bromine to $\alpha\beta$-dichlor- and $\alpha\beta$-dibrombutyric acids. Its methyl ester combines at 180° with sulphur (B. **28**, 1636). When fused with caustic potash, it breaks up into two molecules of acetic acid; nitric acid oxidizes it to acetic and oxalic acids, and potassium permanganate oxidizes it to *dioxybutyric acid* (A. **268**, 7).

(1*a*) α-**Chlorcrotonic Acid**, $CH_3.CH:CCl.CO_2H$, is obtained when trichlorbutyric acid (p. 276) is treated with zinc and hydrochloric acid, or zinc dust and water. Further, by the action of alcoholic potash on $\alpha\beta$-dichlorbutyric ester (B. **21**, R. 243).

(1*b*) β-**Chlorcrotonic Acid**, $CH_3.CCl:CH.CO_2H$, is obtained in small quantities (together with β-chlorisocrotonic acid) from aceto-acetic ester, and by the addition of HCl to tetrolic acid. With boiling alkalies it yields tetrolic acid (p. 288). Sodium amalgam converts both α- and β-chlorcrotonic acids into ordinary crotonic acid.

(1*c*) α-**Bromcrotonic Acid**, from the ester of dibrombutyric acid.

(1*d*) β-**Bromcrotonic Acid**, from tetrolic acid.

Dichlor- and Dibromcrotonic Acids. See tetrolic acid, p. 288.

(2) **Isocrotonic Acid**, *Quartenylic Acid*, *Cis-trans-Crotonic Acid*, *Allocrotonic Acid*, was first obtained from β-chlorisocrotonic acid by the action of sodium amalgam and similarly from the α-chlor-acid. When heated to 170–180°, in a sealed tube, it changes to ordinary crotonic acid. This alteration occurs partially, even during distillation. This explains why, upon fusing isocrotonic acid with KOH, formic and propionic acids (which might be expected) are not produced, but in their stead acetic acid, the decomposition product of crotonic acid. Sodium amalgam does not change it. It combines with HI to yield β-iodo-butyric acid (B. **22**, R. 741). It yields a liquid dichloride, $C_4H_6Cl_2O_2$ (Iso $\alpha\beta$-dichlorbutyric acid), with Cl_2. This passes into α-chlorcrotonic acid. Potassium permanganate oxidizes it to *isodioxybutyric acid* (see this) (A. **268**, 16).

(2*a*) α-**Chlor-isocrotonic Acid** is obtained by the action of sodium hydroxide on free $\alpha\beta$-dichlorbutyric acid. It is the most soluble of the four chlorcrotonic acids (B. **22**, R. 52).

When PCl_5 and water act upon aceto-acetic ester, $CH_3 . CO . CH_2 . CO . C_2H_5$, β-chlorisocrotonic acid (with β-chlorcrotonic acid) is produced. It is very probable that β-dichlorbutyric acid is formed at first, and this afterward parts with HCl. It is also formed by protracted heating of β-chlorcrotonic acid.

Sodium amalgam converts both the α- and β-chlorisocrotonic acid into liquid isocrotonic acid (B. **22**, R. 52).

α-**Bromisocrotonic Acid** is produced by the action of sodium hydroxide upon free $\alpha\beta$-dibrombutyric acid (B. **21**, R. 242).

(3) **Methacrylic Acid**, $CH_2 : C<\genfrac{}{}{0pt}{}{CH_3}{CO_2H}$. Its ethyl ester was first obtained by the action of PCl_3 upon oxy-isobutyric ester, $(CH_3)_2 . C(OH) . CO_2 . C_2H_5$. It is, however, best prepared by boiling citrabrom-pyrotartaric acid (from citraconic acid and HBr) with water or a sodium carbonate solution:

$$C_5H_7BrO_4 = C_4H_6O_2 + CO_2 + HBr.$$

It consists of prisms that are readily soluble in water, fuse at + 16°, and boil at 160.5°. NaHg converts the acid into isobutyric acid. It combines with HBr and HI to form α-brom- and iodo-isobutyric acid, and with bromine to form $\alpha\beta$-dibromisobutyric acid, which confirms the assumed constitution (J. pr. Ch., [2] **25**, 369). When fused with KOH, it breaks up into propionic and acetic acids.

Pentenic Acids, $C_4H_7 . CO_2H$.

Of the isomerides of this formula, angelic or $\alpha\beta$-dimethyl acrylic acid is the most important. It bears the same relation to tiglic acid that was observed with crotonic and isocrotonic acids (p. 282).

1. **Angelic Acid**, $\genfrac{}{}{0pt}{}{H}{CH_3}>C = C<\genfrac{}{}{0pt}{}{CO_2H}{CH_3}$, melting at 45° and boiling at 185°, exists free along with valeric and acetic acids in the roots of *Angelica archangelica*, and as butyl and amyl esters, together with tiglic amyl ester, in Roman oil of cumin, the oil of *Anthemis nobilis*.

Angelic acid congeals, when well cooled, and may be thus separated from liquid valeric acid. We can separate angelic and tiglic acids by means of the calcium salts, that of the first being very readily soluble in cold water (B. **17**, 2261; A. **283**, 105).

When 10 grams of angelic acid are boiled for twenty hours with caustic soda (40 grams NaOH in 160 grams of water), two-thirds of it are converted into tiglic acid. Heating with water at 120° will change half of it to tiglic acid (A. **283**, 108). When pure angelic acid is heated to boiling for hours it is completely changed to tiglic acid. The same occurs by the action of sulphuric acid at 100°. It dissolves without difficulty in hot water, and volatilizes readily in steam. Its *ethyl ester* boils at 141°.

Tiglic Acid, α **Methylcrotonic Acid**, $CH_3 . CH : C<\genfrac{}{}{0pt}{}{CH_3}{CO_2H}$, present in Roman oil of cumin (see above), and in Croton oil (from *Croton tiglium*), is a mixture of glycerol esters of various fatty and oleic acids. It is obtained artificially by acting with PCl_3 upon methyl-ethyl oxy-acetic acid, $_{CH}\genfrac{}{}{0pt}{}{CH_3}{CH_3 . CH_2}>C(OH) . CO_2H$ (its ester).

Tiglic acid melts at 64.5° and boils at 198°. Its *ethyl ester* boils at 152°. Bromine converts it into two *dibromides* (A. **250**, 240; **259**, 1; **272**, 1; **273**, 127; **274**, 99). For their constitution, compare B. **24**, R. 668. The three possible acids, $C_4H_7CO_2H$, with normal structure are also known (Fittig, A. **283**, 47; B. **27**, 2658). *Propilidene Acetic Acid*, $\alpha\beta$-pentenic acid, $CH_3 . CH_2 . CH : CH . CO_2H$., m. p. 10°, b. p. 201°, is formed together with γ-oxyvaleric acid on boiling ethidene propionic acid with soda, as well as with malonic acid, propionic aldehyde and acetic anhydride, together with $\beta\gamma$-pentenic acid. Its *dibromide* melts at 56°. *Ethidene propionic* *acid*, $\beta\gamma$-pentenic acid, $CH_3 . CH : CH . CH_2CO_2H$, b. p. 194°, is best prepared by the distillation of methyl paraconic acid. Its *dibromide* melts at 65°.

Allyl-acetic Acid, $\gamma\delta$-Pentenic Acid, $CH_2 : CH . CH_2 . CH_2 . CO_2H$, obtained on heating allyl malonic acid, boils at 187°.

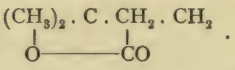
Dimethyl Acrylic Acid, $(CH_3)_2C : CH . CO_2H$, is obtained (1) from β-oxy-isovaleric acid, $(CH_3)_2 . C(OH) . CO_2H$, by distillation; (2) from acetone and malonic acid by means of acetic anhydride (B. **27**, 1574); (3) from its ester, produced when α-brom isovaleric acid ester is heated with diethylaniline (A. **280**, 252). See B. **29**, R. 956, for its derivatives. It melts at 70°.

(4) **Hexenic Acids,** $C_6H_{10}O_2$.

The normal acids belonging in this class are *Hydro-* and *Isohydrosorbic.*

Hydrosorbic Acid, Propylidene-propionic Acid, $\beta\gamma$-hexenic acid, $CH_3 . CH_2 . CH : CH . CH_2 . CO_2H$, boiling at 208°, is obtained from *ethyl-paraconic acid*, $CH_3 . CH_2 . CH . CH(CO_2H)CH_2COO$, according to method 10 (p. 278); hence it is probably a $\beta\gamma$-unsaturated acid. It is the first reduction product of *sorbic acid*, $CH_3CH : CH . CH : CH . CO_2H$. During the reduction a shifting of the double union occurs. On boiling hydrosorbic acid with caustic soda, it passes into the isomeride whose formation one might expect in the reduction of sorbic acid—into **isohydrosorbic acid,** or *butylidene-acetic acid*, *$\alpha\beta$-hexenic acid*, $CH_3CH_2CH_2CH : CHCO_2H$, melting at 33° and boiling at 216° (B. **24**, 83). When its bromine addition product is boiled with water, oxycaprolactone and homolævulinic acid result (A. **268**, 69). *$\gamma\delta$-Hexenic acid*, $CH_3 . CH : CH . CH_2 . CH_2 . CO_2H$, melts at 0°. Consult method of formation 10, page 278. See B. **29**, R. 667 for $\alpha\beta$- and $\beta\gamma$-isohexenic acids.

Pyroterebic Acid, $(CH_3)_2C : CH . CH_2 . CO_2H$, and **Teracrylic Acid,** $C_3H_7 . CH : CH . CH_2 . CO_2H$, b. p. 218° (A. **208**, 37, 39), belong to the acids $C_6H_{10}O_2$ and $C_7H_{12}O_2$. They deserve notice because of their genetic connection with two oxidation products of turpentine oil—*terebic acid* and *terpenylic acid*—which will be considered later. See A. **283**, 129; **288**, 176, for $\beta\gamma$- and *$\alpha\beta$-isoheptenic acids.* Pyroterebic acid is changed by protracted boiling or by HBr to isomeric isocaprolactone:



$$\begin{array}{l}(CH_3)_2 . C . CH_2 . CH_2 \\ \quad\;\, | \qquad\quad\;\; | \\ \quad\;\, O\text{———}CO\end{array} .$$

Teracrylic Acid is converted by HBr into the isomeric lactone of γ-oxyheptoic acid, $C_7H_{13}(OH)O_2$—*heptolactone.*

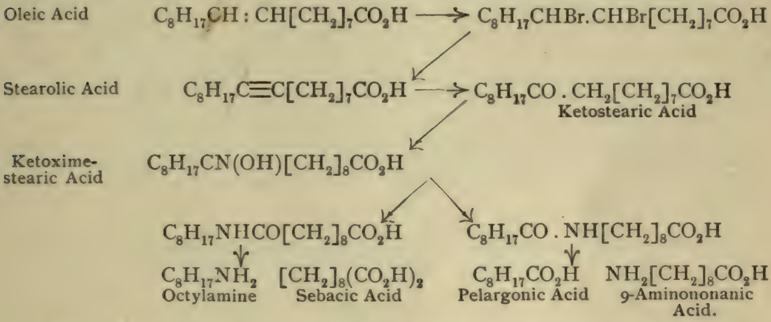
Nonylenic Acid, $CH_3(CH_2)_5CH : CH . CO_2H$, from œnanthol by general method of formation 7, page 277.

Decylenic Acid, $C_6H_{13} . CH = CH . CH_2 . CO_2H$, formed from hexylparaconic acid according to general method of formation 10, page 278.

Undecylenic Acid, $CH_2 = CH(CH_2)_8CO_2H$, is produced by distilling castor oil under reduced pressure. It yields *sebacic acid*, $(CH_2)_8(CO_2H)_2$ (see this) (B. **19**, R. 338; **19**, 2224), upon oxidation. It melts at 24.5°, and boils at 165° (15 mm.). When its dibromide, melting at 38°, is incompletely decomposed by alcoholic potash, *Dehydroundecylenic Acid*, $CH \equiv C[CH_2]_8CO_2H$, melting at 43°, is obtained, which, fused at 180° with caustic potash, changes to *Undecolic Acid*, $CH_3 . C \vdots C[CH_2]_7CO_2H$, melting at 59° (B. **29**, 2232).

Higher Olefine Monocarboxylic Acids.

To ascertain the point of the doubly linked carbon atoms in the higher olefine monocarboxylic acids, the latter are converted into their corresponding acetylene monocarbonic acids (p. 287), which, in turn, are oxidized and split open at the point of triple carbon union, or they are changed to ketone carboxylic acids, and these are then broken down. Thus, oleic acid yields *stearolic acid*, which may be oxidized to *azelaic acid*, $C_7H_{13}(CO_2H)_2$, and *pelargonic acid*, $C_8H_{17}CO_2H$. This would mean that in stearolic acid the carbon atoms 9 and 10 are united by three bonds, and that they are the atoms which in oleic acid are in double union. This conclusion is confirmed by the conversion of stearolic acid, by means of concentrated sulphuric acid, into *ketostearic* acid, whose oxime undergoes the Beckmann rearrangement at 400°, as the result of the action of concentrated sulphuric acid. Two acid amides result, which are decomposed by fuming hydrochloric acid, the one into octylamine and sebacic acid, the other into pelargonic acid and 9-aminononanic acid (B. **27**, 172):



The constitution of hypogæic and erucic acids has been determined in the same manner.

Hypogæic Acid, $CH_3[CH_2]_7CH:CH[CH_2]_5CO_2H$, found as glycerol ester in earthnut oil (from the fruit of *Arachis hypogæa*), crystallizes in needles, and melts at 33° and boils at 236° (15 mm.). It results when stearolic acid is fused with KOH at 200° (B. **27**, 3397).

Oleic Acid, *Olein Acid*, $\begin{smallmatrix}C_8H_{17}\\H\end{smallmatrix}\!>C:C<\!\begin{smallmatrix}H\\[CH_2]_7CO_2H\end{smallmatrix}=C_{18}H_{34}O_2$, melting at 14° and boiling at 223° (10 mm.), occurs as glycerol ester (*triolein*) in nearly all fats, especially in the oils, as olive oil, almond oil, cod-liver oil, etc. It is obtained in large quantities as a by-product in the manufacture of stearin candles (p. 253).

In preparing oleic acid, olive or mandel oil is saponified with potash and the aqueous solution of the potassium salts precipitated with sugar of lead. The lead salts which separate are dried and extracted with ether, when lead oleate dissolves, leaving as insoluble the lead salts of all other fatty acids. Mix the ethereal solution with hydrochloric acid, filter off the lead chloride, and concentrate the liquid. To purify the acid obtained in this way, fractionate it under strongly diminished pressure.

Oleic acid in a pure condition is odorless, and does not redden litmus. On exposure to the air it oxidizes, becomes yellow, and acquires a rancid odor. Nitric acid oxidizes it with formation of all the lower fatty acids from *capric* to *acetic*, and at the same time dibasic acids, like sebacic acid, are produced. A permanganate solution oxidizes it to azelaic acid, $C_9H_{16}O_4$. Moderated oxidation produces dioxystearic acid (see this).

It unites with bromine to form liquid dibromstearic acid, $C_{18}H_{34}Br_2O_2$, which is converted by alcoholic KOH into *monobromoleic acid*, $C_{19}H_{33}BrO_2$, and then into stearoleic acid (p. 288).

Nitrous acid changes oleic into the isomeric crystalline

Elaïdic Acid, $\begin{matrix}C_8H_{17}\\H\end{matrix}>C:C<\begin{matrix}[CH_2]_7CO_2H\\H\end{matrix}$, melting at 51° and boiling at 225° (10 mm.). With bromine it yields the dibromide, $C_{18}H_{34}Br_2O_2$, which melts at 27°, and when acted upon with sodium amalgam, passes back into elaïdic acid.

Iso-oleic acid, $C_{18}H_{34}O_2$, melting at 44–45°, is obtained from the HI-addition product of oleic acid—iodostearic acid—when it is treated with alcoholic potash, or from oxystearic acid, formed from oleic acid by the action of conc. sulphuric acid, when it is distilled under reduced pressure (B. **21**, R. 398; **21**, 1878; **27**, R. 576).

Hydriodic acid reduces oleic and elaïdic acids to *stearic acid*. Oleic, elaïdic, and iso-oleic acids, when fused with caustic potash, break down into *palmitic acid* and *acetic acid*. This is, however, a reaction that can not be accepted as proving that the double union in the three acids holds the same position. The common view is that oleic and elaïdic acids are stereo-isomerides, and that iso-oleic is a structural isomeride of the other two acids.

Bromine converts the three acids into three different *dibrom-stearic acids*. Carefully oxidized with potassium permanganate, they yield three different *dioxystearic acids*.

Erucic Acid, $\begin{matrix}C_8H_{17}\\H\end{matrix}>C:C<\begin{matrix}H\\C_{11}H_{22}CO_2H\end{matrix}$, *Brassidic Acid,* $\begin{matrix}H\\C_8H_{17}\end{matrix}>C:C<\begin{matrix}H\\C_{11}H_{22}CO_2H\end{matrix}$, is present as glyceride in rape-seed oil (from *Brassica campestris*), in the fatty oil of mustard, and in the oil of grape seeds. It melts at 33°–34°.

Nitrous acid (B. **19**, 3320) converts erucic acid into isomeric *brassidic acid*, melting at 66° and boiling at 256° (10 mm.). It sustains the same relation to erucic acid that elaïdic does to oleic (p. 285). By oxidation, erucic acid yields nonylic and brassylic acids (B. **24**, 4120; **25**, 961, 2667; **26**, 639, 838, 1867, R. 795, 811). *Iso-erucic Acid*, see B. **27**, R. 166, 577.

Linoleic and ricinoleic acids, although not belonging to the same series, yet closely resemble oleic acid. The first is a simple, unsaturated acid, the second an unsaturated oxy-acid.

Linoleic Acid, $C_{18}H_{32}O_2$, occurs as glyceride in *drying oils*, which quickly oxidize in the air, become covered with a scum, and then solidify—*e. g.*, linseed oil, hemp oil, poppy oil, and nut oil. In the *non drying* oils—olive oil, rape-seed oil from *Brassica campestris*, the oil from *Brassica rapa*, mandel oil, fish oil, etc.—we have the oleic glycerol ester.

Various oxy-fatty acids are produced when linoleic acid is oxidized with potassium permanganate. From the fact that they can be formed, it has been concluded that certain other acids exist in the crude linoleic acid (B. **21**, R. 436 and 659).

Ricinoleic Acid, $CH_3[CH_2]_5 . CHOH . CH_2 . CH : CH(CH_2)_7\text{-}CO_2H [\alpha]_D = +6.67°$ (B. **27**, 3471), is present in castor oil in the form of a glyceride. The lead salt is soluble in ether. Subjected to dry distillation, ricinoleic acid splits into *œnanthol*, $C_7H_{14}O$, and *undecylenic acid*, $C_{11}H_{20}O_2$.

Fused with caustic potash, it changes to *sebacic acid*, $C_8H_{16}(CO_2H)_2$, and *secondary octyl alcohol*, $\begin{matrix}C_6H_{13}\\CH_3\end{matrix}>CH . OH$. It combines with bromine to a solid *dibromide*. When heated with HI (iodine and phosphorus), it is transformed into iodoleic acid, $C_{18}H_{33}IO_2$, which yields stearic acid when treated with zinc and hydrochloric acid (B. **29**, 806).

The point of double union between the carbon atoms in ricinoleic acid is ascertained as in the case of oleic acid:

(1) By transposition into *ricinstearolic acid*, melting at 53°; (2) and this into *keto-oxystearic acid*, melting at 84°; (3) finally, the breaking-down of the oxime of the latter acid (B. **27**, 3121).

Nitrous acid converts ricinoleic acid into isomeric *ricinelaïdic acid*. This melts at 53° C. (see B. **21**, 2735; **27**, R. 629).

Rapinic Acid, $C_{18}H_{34}O_2$, occurs as glycerol ester in rape oil (B. **29**, R. 673).

Unsaturated Acids, $C_nH_{2n-3}CO_2H$.

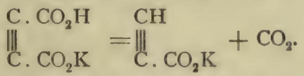
The acids of this series contain either a trebly linked pair of carbon atoms, *e. g.*, like *acetylene* (p. 95), or two doubly linked pairs of carbon atoms, as in the *diolefines*. They are, therefore, distinguished as acetylene monocarboxylic acids: *propiolic acid series* and *diolefine monocarboxylic acids*.

C. ACETYLENE CARBOXYLIC ACIDS.

Methods of Formation.—1. (*a*) By the action of alcoholic potash upon the brom-addition products of the oleic acids, and (*b*) the monohalogen substitution products of the oleic acids. This is similar to the formation of the acetylenes from the dihalogen addition products and the monohalogen substitution products.

2. From the sodium derivatives of the mono-alkyl acetylenes by the action of CO_2: $CH_3 . C \equiv CNa + CO_2 = CH_3C \equiv C . CO_2Na$. Like the acetylenes, they are capable of saturating 2 and 4 univalent atoms.

Propiolic Acid, $CH \vdots C . CO_2H$, **Propargylic Acid** [Propin-Acid], melting at + 6° and boiling with decomposition at 144° (p. 132), corresponds to propargyl alcohol. The *potassium salt*, $C_3HKO_2 + H_2O$, is produced from the primary potassium salt of acetylene dicarboxylic acid, when its aqueous solution is heated:



$$\begin{array}{l} C . CO_2H \\ \| \! | \\ C . CO_2K \end{array} = \begin{array}{l} CH \\ \| \! | \\ C . CO_2K \end{array} + CO_2.$$

Acetic acid results in like manner from malonic acid (p. 244).

The aqueous solution of the salt is precipitated by ammoniacal silver and cuprous chloride solutions, with formation of explosive metallic derivatives. By prolonged boiling with water the potassium salt is decomposed into acetylene and potassium carbonate.

Free propiolic acid, liberated from the potassium salt, is a liquid with an odor resembling that of glacial acetic acid. The acid dissolves readily in water, alcohol, and ether, and reduces silver and platinum salts. Exposed to sunlight (away from air contact) it polymerizes to trimesic acid, $3C_2H . CO_2H = C_6H_3(CO_2H)_3$. Sodium amalgam converts it into propionic acid. It forms β-halogen acrylic acids with the halogen acids (p. 281) (B. **19**, 543), and with the halogens yields $\alpha\beta$-dihalogen-acrylic acids.

The *ethyl ester* boils at 119°. With ammoniacal cuprous chloride it unites to a stable yellow-colored compound. Zinc and sulphuric acid reduce it to ethyl propargylic ester (p. 136) (B. **18**, 2271).

Chlorpropiolic Acid, $CCl \equiv C . CO_2H$, and **Brompropiolic Acid**, C_3BrHO_2, have been obtained as barium salts from dichloracrylic and mucobromic acids,

$C_3H_2Cl_2O_2$ and $C_4H_2Br_2O_3$. **Iodopropiolic Acid** is obtained by saponifying its ethyl ester, melting at 68°. It melts at 140°. The ethyl ester may be prepared from the Cu derivative of propiolic ester (see above) by the action of iodine.

The three acids decompose readily into carbon dioxide and spontaneously inflammable *chloracetylene*, $CCl\equiv CH$, *bromacetylene* and *iodoacetylene*. The addition of haloid acids leads to $\beta\beta$-dihalogen-acrylic acids, while the halogens form *trihalogen-acrylic acids*.

Carbon dioxide converts the sodium compounds of the corresponding alkyl acetylenes into the following homologues of propiolic acid (B. **12**, 853; J. pr. Ch. [2] **37**, 417):

		M. P.	B. P.
Tetrolic Acid, *Methyl-acetylene Carboxylic Acid*	$CH_3C\equiv C.CO_2H$	76°	203°
Ethyl-acetylene Carboxylic Acid	$CH_3.CH_2.C\equiv C.CO_2H$	80°	—
n-Propyl-acetylene Carboxylic Acid	$CH_3.CH_2.CH_2.C\equiv C.CO_2H$	27°	125° (20 mm.)
Isopropyl-acetylene Carboxylic Acid	$(CH_3)_2CH.C\equiv C.CO_2H$	38°	107° (20 mm.)
n-Butyl-acetylene Carboxylic Acid	$CH_3.[CH_2]_3C\equiv C.CO_2H$	liquid	136° (20 mm.)

Of these, **Tetrolic Acid** has been the most thoroughly investigated, and is obtained from β chlorcrotonic acid and β-chlorisocrotonic acid when these are boiled with potash. At 210° the acid decomposes into CO_2 and allylene, C_3H_4 (B. **27**, R. 751). Potassium permanganate oxidizes it to acetic and oxalic acids. It combines with HCl and HBr, forming β-chlorcrotonic acid and β-bromcrotonic acid (B. **22**, R. 51; **21**, R. 243). With bromine, in sunlight, it yields *dibromcrotonic acid*, melting at 120°, whereas in the dark the halogen produces a dibrom-acid, melting at 94° (B. **28**, 1877). $\alpha\beta\beta$-Trichlorbutyric acid (p. 276) upon the loss of HCl yields two *dichlorcrotonic acids*, one melting at 75° and the other at 92° (B. **28**, 2665). These are two acids which are produced when chlorine acts upon tetrolic acid.

Several higher homologues of propiolic acid have been prepared by the action of alcoholic potash upon the brom-addition products of the higher olefine monocarboxylic acids (p. 278):

Undecolic Acid, $C_{11}H_{18}O_2$, obtained from undecylenic acid (p. 284), fuses at 59.5°. **Stearolic Acid**, $C_{18}H_{32}O_2$ (constitution, see p. 285), is obtained from oleic and elaïdic acids. It melts at 48°. **Behenolic Acid**, $C_{22}H_{40}O_2$ (constitution, see p. 286), from the bromides of erucic and brassidic acids, melts at 57.5°. On warming the last two acids with fuming nitric acid they yield the monobasic acids: *stearoxylic*, or 9.10-*dioxystearic acid*, $CH_3[CH_2]_7CO.CO[CH_2]_7CO_2H$, melting at 86°, and *behenoxylic*, or 13.14-*dioxobehenic acid*, $CH_3[CH_2]_7CO.CO.[CH_2]_{11}CO_2H$, melting at 96° (B. **28**, 276).

Sulphuric acid converts stearolic acid into ketostearic acid, and behenolic acid into ketobrassidic acid (B. **26**, 1867), whose oximes are then transposed by the sulphuric acid into $C_8H_{17}CO.NH[CH_2]_8CO_2H$ (p. 285). (Oxidation, compare erucic and brassidic acids, p. 286.)

D. DIOLEFINE CARBOXYLIC ACIDS.

Butdiëne Carboxylic Acid, $CH_2:CH.CH:CHCO_2H$, melting at 102°, is formed, together with ethidene propionic acid (p. 283), by the reduction of *perchlorbutdiëne carboxylic acid*, $CCl_2:CCl.CCl:CCl.CO_2H$, melting at 97°, and *perchlorbutine* *carboxylic acid*, $CCl_3 . C \vdots C . CCl_2 . CO_2H$, melting at 127°. These are products of decomposition resulting from the two hexa-chlor-R-pentenes upon treatment with alkali (B. **28**, 1644).

Sorbic Acid, $CH_3CH : CH . CH : CH . CO_2H$, is obtained from sobinol, a lactone of *parasorbic acid* (see this), occurring, together with malic acid, in the juice of unripe mountain-ash berries (from *Sorbus aucuparia*) (A. **110**, 129), on boiling with caustic soda, or with hydrochloric acid (B. **27**, 351). Potassium permanganate oxidizes it to aldehyde and racemic acid (see this), which establishes the constitution of the acid (B. **23**, 2377; **24**, 85):

$$\underset{\text{Sorbic Acid}}{CH_3.CH:CH.CH:CH.CO_2H} + H_2O + 4O = CH_3.CHO + \underset{\text{Racemic Acid.}}{CO_2H.(CH.OH)_2.CO_2H.}$$

The *ethyl ester* boils at 195°. Nascent hydrogen converts the acid into *hydrosorbic acid*.

Diallylacetic Acid, $(CH_2 : CH . CH_2)_2CH . CO_2H$, is obtained from ethyl diallylaceto-acetate and diallyl malonic acid. It boils at 227°. Nitric acid oxidizes it to tricarballylic acid, $(CO_2H . CH_2)_2CHCO_2H$).

Geranic Acid belongs to the class of olefine dicarboxylic acids. It will be described together with the olefine terpene bodies.

IV. DIHYDRIC ALCOHOLS OR GLYCOLS, AND THEIR OXIDATION PRODUCTS.

The monohydric alcohols, with their oxidation products,—the aldehydes, the ketones, and the monocarboxylic acids, with their derivatives,—were discussed in the preceding section.

Closely allied to these are the *dihydric alcohols* or *glycols*, and such compounds as may be considered oxidation products of the *glycols*.

The glycols are derived from the hydrocarbons by the replacement of two hydrogen atoms attached to two different carbon atoms by two hydroxyls. In the case of the monohydric alcohols we distinguished three classes—primary, secondary, and tertiary alcohols. With the *glycols* the classes are twice as numerous. The compounds, which may be considered as oxidation products of the glycols, contain either *two similar*, reactive, atomic groups—*e. g.*:

the *dialdehydes* (*glyoxal*, $CHO.CHO$),
the *diketones* (*diacetyl*, $CH_3 . CO . CO . CH_3$),
the *dicarboxylic acids* (*oxalic acid*, $COOH . COOH$),

and therefore manifest double the typical properties of the oxidation products of the monohydric alcohols—compounds of *double function*; or they contain *two* different reactive atomic groups in the same molecule, and have, therefore, the typical properties of different families of compounds. The following bodies have such a *mixed function:*

Aldehyde Alcohols (*Glycolylaldehyde*, $CH_2OH . CHO$)
Ketone Alcohols (*Acetylcarbinol*, $CH_2OH . CO . CH_3$)
Aldehyde Ketones (*Pyroracemic Aldehyde*, $CH_3 . CO . CHO$)
Alcohol Acids or *Oxyacids* (*Glycollic Acid*, $CH_2 . OH . COOH$)
Aldehydic Acids (*Glyoxylic Acid*, $CHO . CO_2H$)
Ketonic Acids (*Pyroracemic Acid*, $CH_3CO . COOH$).

Four families—alcohols, aldehydes, ketones, and monocarboxylic acids—occur with the monohydric alcohols and their oxidation products, while in the case of the dihydric alcohols and their oxidation products *ten* classes of derivatives are known. The successive series in which these ten classes will be discussed readily follow, if their systematic interdependence be developed similarly to that of the univalent alcohols and their oxidation products.

MONOHYDRIC ALCOHOLS AND THEIR OXIDATION PRODUCTS.

1*a*. Primary Alcohols, 1*b*. Secondary " 1*c*. Tertiary "	2. Aldehydes, 3. Ketones,	4. Monocarboxylic Acids.

DIHYDRIC ALCOHOLS AND THEIR OXIDATION PRODUCTS.

1*a*. Diprimary **Glycols**,	2*a*. prim. **Oxyaldehydes**,	7*a*. prim. **Oxycarboxylic Acids**,
	4. **Dialdehydes**,	8. **Aldehydocarboxylic Acids**,
		10. **Dicarboxylic Acids**,
$\begin{array}{l}CH_2 . OH\\ \dot{C}H_2 . OH\end{array}$ Glycol	$\begin{array}{l}CHO\\ \dot{C}H_2OH\end{array}$ Glycolylaldehyde	$\begin{array}{l}COOH\\ \dot{C}H_2 . OH\end{array}$ Glycollic Acid
	$\begin{array}{l}CHO\\ \dot{C}HO\end{array}$ Glyoxal	$\begin{array}{l}CO_2H\\ \dot{C}HO\end{array}$ Glyoxylic Acid $\begin{array}{l}COOH\\ \dot{C}OOH\end{array}$ Oxalic Acid
1*b*. Prim. sec. Glycols,	2*b*. sec. **Oxyaldehydes**, 3*a*. prim. **Oxyketones**, 5. **Aldehydketones**,	7*b*. sec. Oxycarboxylic Acids, 9. **Ketone Carboxylic Acids**,
1*c*. Prim. tert. Glycols, 1*d*. Disecond. Glycols,	2*c*. tert. Oxyaldehydes, 3*b*. sec. Oxyketones, 6. **Diketones**,	7*c*. tert. Oxycarboxylic Acids.
1*e*. Sec. tert. Glycols, 1*f*. Ditert. Glycols.	3*c*. tert. Oxyketones.	

The dihydric alcohols and their oxidation products will be described and discussed in the following order:

1. *Glycols, Diacid alcohols.*

2. Oxyaldehydes, *Aldehyde alcohols.* 3. Oxyketones, *Ketone alcohols.*

4. Dialdehydes. 5. Aldehyde ketones. 6. Diketones.

7. Oxyacids, *Alcohol monocarboxylic acids.*

8. Aldehyde monocarboxylic acids. 9. Ketomonocarboxylic acids. 10. Dicarboxylic acids.

From the very nature of the conditions there are no compounds in any of these series which contain but one carbon atom in the molecule. However, carbonic acid with its exceedingly numerous derivatives will be introduced before the dicarboxylic acids—the *carbonic acid group.*

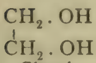
Carbonic acid is the simplest dibasic acid; it is similar, in many respects, to the dicarboxylic acids and a special type for such acids, which, like it, only occur in an anhydride form. Formic acid, the simplest acid, showing, at one and the same time, the character of an aldehyde and a monocarboxylic acid, might, for the very same reason, have been placed before *glyoxylic acid*, at the head of the aldehyde acids. However, it is customary to place formic acid at the head of the fatty acids, because the acid nature in it appears more frequently than does its aldehyde character.

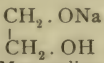
1. DIHYDRIC ALCOHOLS OR GLYCOLS.

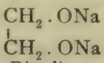
A. PARAFFIN GLYCOLS.

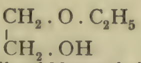
Würtz (1856) discovered glycol, and thus succeeded in filling out the gap between the monohydric alcohols and the triacid alcohol, glycerol. Würtz chose the name glycol to indicate the relation of the new body to alcohol on the one hand and glycerol on the other. Glycols are distinguished as α-, β-, γ-, δ-, etc., according as the hydroxyls are attached to adjacent carbon atoms, or in 1.3-, 1.4-, and 1.5- positions respectively. There are also diprimary, primary-secondary, etc., glycols (consult p. 290). The Geneva names are obtained for the glycols by attaching the final syllable "diol" to the name of the parent hydrocarbon.

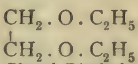
Glycols differ from the monohydric alcohols just as the oxyhydrates of bivalent metals differ from those of univalent metals, or as a dibasic acid from a monobasic acid. As a rule, the reactions leading from the monohydric alcohols and glycols to their corresponding derivatives are very similar. It is only in the case of the two hydroxyl groups of the glycols that they are able to successively pass to completion, and in so doing they give rise first to substances which still show the character of a monohydric alcohol. Take ethylene glycol, for example: it is capable of forming a mono- and dialkali glycollate, corresponding to the alcoholates of the monohydric alcohols, mono- and dialkyl ethers, mono- and dihalogen esters, nitric acid esters and esters of organic acids, *e.g.*:

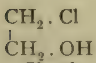

$\begin{array}{l}CH_2.OH\\ |\\ CH_2.OH\end{array}$
Glycol

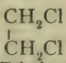

$\begin{array}{l}CH_2.ONa\\ |\\ CH_2.OH\end{array}$
Monosodium Glycollate

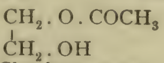

$\begin{array}{l}CH_2.ONa\\ |\\ CH_2.ONa\end{array}$
Disodium Glycollate

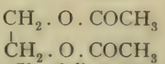

$\begin{array}{l}CH_2.O.C_2H_5\\ |\\ CH_2.OH\end{array}$
Glycol Mono-ethyl Ether


$\begin{array}{l}CH_2.O.C_2H_5\\ |\\ CH_2.O.C_2H_5\end{array}$
Glycol Diethyl Ether


$\begin{array}{l}CH_2.Cl\\ |\\ CH_2.OH\end{array}$
Glycol-chlorhydrin

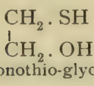

$\begin{array}{l}CH_2Cl\\ |\\ CH_2Cl\end{array}$
Ethylene Chloride


$\begin{array}{l}CH_2.O.COCH_3\\ |\\ CH_2.OH\end{array}$
Glycol-monacetate


$\begin{array}{l}CH_2.O.COCH_3\\ |\\ CH_2.O.COCH_3\end{array}$
Glycol-diacetate.

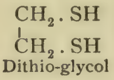
All the mono-compounds also manifest the character of monohydric alcohols; they and the di compounds, which have been mentioned, can be obtained from the glycols by the same methods as the corresponding transposition products of the monohydric alcohols.

The sulphur- and nitrogen-containing derivatives of the glycols correspond to like derivatives of the monacid alcohols:



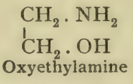
$$\begin{array}{l} CH_2.SH \\ | \\ CH_2.OH \end{array}$$

Monothio-glycol



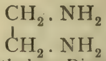
$$\begin{array}{l} CH_2.SH \\ | \\ CH_2.SH \end{array}$$

Dithio-glycol



$$\begin{array}{l} CH_2.NH_2 \\ | \\ CH_2.OH \end{array}$$

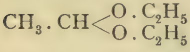
Oxyethylamine



$$\begin{array}{l} CH_2.NH_2 \\ | \\ CH_2.NH_2 \end{array}$$

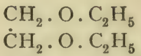
Ethylene Diamine.

The aldehydes have been repeatedly spoken of as the anhydrides of diacid alcohols, in which the two hydroxyl groups are joined to the *same carbon atom*, and which can only exist under special conditions. Yet, the ethers or acetals, esters and other derivatives of these hypothetical compounds are stable. These bodies are naturally isomeric with the corresponding derivatives of the diacid alcohols, in which the hydroxyls are attached to *different carbon atoms*. The following, for example, are isomeric:



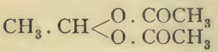
$$CH_3.CH<\begin{array}{l} O.C_2H_5 \\ O.C_2H_5 \end{array}$$

Acetal and



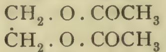
$$\begin{array}{l} CH_2.O.C_2H_5 \\ \dot{C}H_2.O.C_2H_5 \end{array}$$

Glycoldiethyl Ether



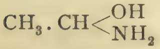
$$CH_3.CH<\begin{array}{l} O.COCH_3 \\ O.COCH_3 \end{array}$$

Ethidene Diacetate and



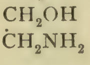
$$\begin{array}{l} CH_2.O.COCH_3 \\ \dot{C}H_2.O.COCH_3 \end{array}$$

Glycol Diacetate



$$CH_3.CH<\begin{array}{l} OH \\ NH_2 \end{array}$$

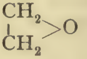
Aldehyde Ammonia and



$$\begin{array}{l} CH_2OH \\ \dot{C}H_2NH_2 \end{array}$$

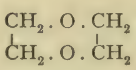
Oxyethylamine.

The *cyclic derivatives of the glycols* are extremely characteristic. Thus, glycol yields two cyclic ethers:



$$\begin{array}{l} CH_2 \\ | \\ CH_2 \end{array}\!\!>O$$

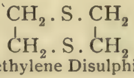
Ethylene Oxide



$$\begin{array}{l} CH_2.O.CH_2 \\ |\qquad\quad | \\ CH_2.O.CH_2 \end{array}$$

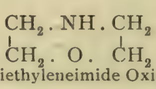
Diethylene Oxide,

and also sulphur- and nitrogen-compounds corresponding to diethylene oxide:



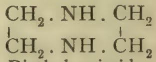
$$\begin{array}{l} CH_2.S.CH_2 \\ |\qquad\quad | \\ CH_2.S.CH_2 \end{array}$$

Diethylene Disulphide



$$\begin{array}{l} CH_2.NH.CH_2 \\ |\qquad\qquad | \\ CH_2.\ O.\ CH_2 \end{array}$$

Diethyleneimide Oxide



$$\begin{array}{l} CH_2.NH.CH_2 \\ |\qquad\qquad | \\ CH_2.NH.CH_2 \end{array}$$

Diethyleneimide.

Methods of Formation.—The first three methods proceed from the olefines, and lead, according to the constitution of the latter, to glycols of every description.

The halogen addition products of the olefines—the alkylen haloids—may be regarded as the *haloid acid esters* of the glycols. When these are acted upon by alkalies, with the purpose of exchanging hydroxyl for their halogen, they split off a halogen hydride and pass first into monohalogen olefines and then into acetylenes. It was Würtz who observed that it was only necessary to treat the alkylen haloids with acetates in order to reach the acetic esters of the glycols, and then, by saponification with alkalies, to obtain the glycols.

(1) By heating the alkylen haloids (p. 102) with silver acetate (and glacial acetic acid), or with potassium acetate in alcoholic solution:

$$C_2H_4I_2 + 2C_2H_3O_2 . Ag = \underset{\text{Ethylene Diacetate.}}{C_2H_4{<}\begin{smallmatrix} O . C_2H_3O \\ O . C_2H_3O \end{smallmatrix}} + 2AgI.$$

Inasmuch as the alkylens are made from monohydric alcohols by the withdrawal of water, and are transformed by the addition of halogens into alkylen haloids, the preceding reaction may be regarded as a method of converting monohydric alcohols into dihydric alcohols or glycols. The resulting acetic esters are purified by distillation, and then saponified by KOH or baryta water:

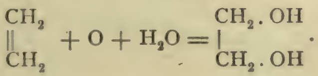
$$C_2H_4{<}\begin{smallmatrix} O . C_2H_3O \\ O . C_2H_3O \end{smallmatrix} + 2KOH = C_2H_4{<}\begin{smallmatrix} OH \\ OH \end{smallmatrix} + 2C_2H_3O_2K.$$

A direct conversion of alkylen haloids into glycols may be attained by heating them with water (A. **186**, 293), with water and lead oxide, or sodium and potassium carbonate.

(2) Another procedure consists in shaking the alkylens, C_nH_{2n}, with aqueous hypochlorous acid, and afterward decomposing the chlorhydrins formed with moist silver oxide:

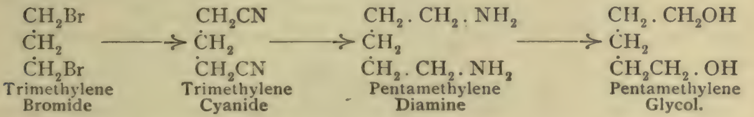
$$C_2H_4 + ClOH = C_2H_4{<}\begin{smallmatrix} Cl \\ OH \end{smallmatrix} \text{ and}$$
$$C_2H_4{<}\begin{smallmatrix} Cl \\ OH \end{smallmatrix} + AgOH = C_2H_4{<}\begin{smallmatrix} OH \\ OH \end{smallmatrix} + AgCl.$$

(3) By the oxidation of the olefines (*a*) in alkaline solution (p. 93, Wagner, B. **21**, 1230) with potassium permanganate; (*b*) with hydrogen peroxide. Thus, ethylene yields *ethylene glycol*; isobutylene, *isobutylene glycol*, $(CH_3)_2 . C(OH) . CH_2 . OH$:



$$\begin{array}{l} CH_2 \\ \| \\ CH_2 \end{array} + O + H_2O = \begin{array}{l} CH_2 . OH \\ | \\ CH_2 . OH \end{array}.$$

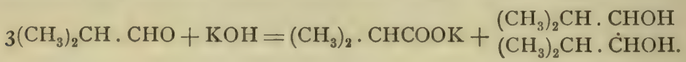
(4) By the action of nitrous acid on diamines (p. 166). As these diamines can be obtained from the corresponding nitriles of dibasic acids, and the nitriles themselves from alkylen haloids, therefore these reactions not only ally the classes of derivatives mentioned, but they afford a means of building up the glycols:



$$\begin{array}{ccccccc} \begin{array}{l} CH_2Br \\ \dot{C}H_2 \\ \dot{C}H_2Br \end{array} & \longrightarrow & \begin{array}{l} CH_2CN \\ \dot{C}H_2 \\ \dot{C}H_2CN \end{array} & \longrightarrow & \begin{array}{l} CH_2 . CH_2 . NH_2 \\ \dot{C}H_2 \\ \dot{C}H_2 . CH_2 . NH_2 \end{array} & \longrightarrow & \begin{array}{l} CH_2 . CH_2OH \\ \dot{C}H_2 \\ \dot{C}H_2CH_2 . OH \end{array} \\ \text{Trimethylene} & & \text{Trimethylene} & & \text{Pentamethylene} & & \text{Pentamethylene} \\ \text{Bromide} & & \text{Cyanide} & & \text{Diamine} & & \text{Glycol.} \end{array}$$

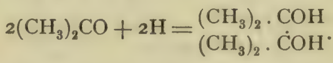
(5) Some glycols have been prepared by the reduction of the corresponding aldehydes or ketones; thus, *αγ-butylene glycol* by the reduction of *aldol*; *αδ-hexylene glycol* from *γ-acetobutyl-alcohol*), etc.

Nucleus-synthetic Methods.—(6) *Disecondary glycols* are produced on treating certain aldehydes with alcoholic potash, when two aldehyde molecules are reduced to a disecondary glycol, and one is oxidized to the corresponding carboxylic acid (B. **29**, R. 350). Isobutyraldehyde yielded symmetrical *di-isopropyl ethylene glycol:*



$$3(CH_3)_2CH\,.\,CHO + KOH = (CH_3)_2\,.\,CHCOOK + \begin{array}{l}(CH_3)_2CH\,.\,CHOH\\ (CH_3)_2CH\,.\,\dot{C}HOH.\end{array}$$

(7) *Ditertiary glycols* result, together with secondary alcohols, in the reduction of ketones (p. 212). In this manner *pinacone* or *tetramethyl-ethyl glycol* (p. 296) was made from acetone (Friedel):



$$2(CH_3)_2CO + 2H = \begin{array}{l}(CH_3)_2\,.\,COH\\ (CH_3)_2\,.\,\dot{C}OH\end{array}\cdot$$

Properties.—The glycols are neutral, thick liquids, holding, as far as their properties are concerned, a place intermediate between the monohydric alcohols and trihydric glycerol. The solubility of a compound in water increases according to the accumulation of OH groups in it, and it will be correspondingly less soluble in alcohol, and especially in ether. There will be also an appreciable rise in the boiling temperature, while the body acquires at the same time a sweet taste, inasmuch as there occurs a gradual transition from the hydrocarbons to the sugars. In accord with this, the glycols have a sweetish taste, are very easily soluble in water, slightly soluble in ether, and boil much higher (about 100°) than the corresponding monohydric alcohols.

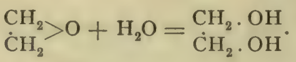
Behavior.—(1) With dehydrating agents, see alkylen oxides: cyclic esters of the glycols. 2d Method of formation, page 298.

(2) Many glycols, when oxidized, especially the primary, pass into the corresponding oxidation products; see ethylene glycol; others break down with the splitting-off of carbon chains.

(3) Conduct toward the haloid acids, nitric acid, concentrated sulphuric acid, acid chlorides and acid anhydrides; see esters of the glycols, page 300.

1. **Ethylene Glycol,** [1.2-Ethandiol], $CH_2OH\,.\,CH_2OH$, melting at —11.5°, boiling at 197.5°, with a specific gravity of 1.125(0°), is miscible with water and alcohol. Ether dissolves but small quantities of it.

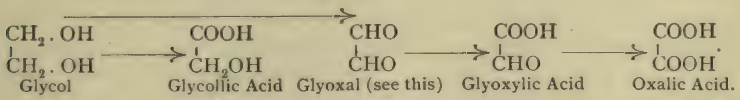
It may be obtained from ethylene through ethylene bromide (ethylene chloride) [general method of formation, p. 293] or by direct oxidation, and also from ethylene oxide by the absorption of water:



$$\begin{array}{l}CH_2\\ \dot{C}H_2\end{array}\!\!>O + H_2O = \begin{array}{l}CH_2\,.\,OH\\ \dot{C}H_2\,.\,OH\end{array}.$$

Preparation.—Boil 188 grams ethylene bromide, 133 grams K_2CO_3 and 1 liter of water, with a return condenser, until all the ethylene bromide is dissolved (A. **192**, 240 and 250). It would be more advantageous to take a little water and add ethylene bromide and the carbonate in portions, filtering from time to time from the separated potassium bromide.

Deportment.—(1) On heating ethylene glycol with zinc chloride water is eliminated and acetaldehyde (and crotonaldehyde) formed. (2) Nitric acid oxidizes glycol to glycollic acid and glyoxal, glyoxylic acid and oxalic acid. The first oxidation product, glycolaldehyde (see this), is further oxidized too rapidly:



$$\begin{array}{l}CH_2.OH\\|\\CH_2.OH\end{array} \longrightarrow \begin{array}{l}COOH\\|\\CH_2OH\end{array} \quad \begin{array}{l}CHO\\|\\CHO\end{array} \longrightarrow \begin{array}{l}COOH\\|\\CHO\end{array} \longrightarrow \begin{array}{l}COOH\\|\\COOH\end{array}$$

Glycol — Glycollic Acid — Glyoxal (see this) — Glyoxylic Acid — Oxalic Acid.

(3) And when glycol is heated, together with caustic potash, to 250°, it is oxidized to oxalic acid with evolution of hydrogen.

(4) Heated to 160° with concentrated hydrochloric acid, *glycolchlorhydrin* results; which at 200° is converted into *ethylene chloride*.

(5) The latter is also produced when PCl_5 acts upon glycol.

(6) Nitric-sulphuric acid changes glycol to *glycol dinitrate*.

(7) Concentrated sulphuric acid and glycol yield *glycol sulphate*.

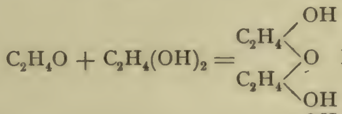
(8) The acid chlorides or acid anhydrides produce mono- and di-esters of glycol.

Glycollates:

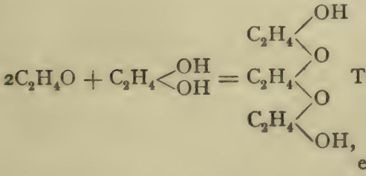
Metallic sodium dissolves in glycol, forming sodium glycollate, $C_2H_4{<}^{OH}_{ONa}$, and (at 170°) disodium glycollate, $C_2H_4(ONa)_2$. Both are white, crystalline bodies, regenerating glycol with water. The alkylogens convert them into ethers.

Polyethylene Glycols:

Ethylene oxide absorbs water and becomes glycol. The latter and ethylene oxide unite at 100° in varying proportions, thus yielding the polyethylene glycols:



Diethylene glycol, b. p., 250°.



Triethylene glycol, b. p., 287°.

The polyglycols are thick liquids, with high boiling points. They behave like the glycols. *Ether-acids* may be obtained from them by oxidation with dilute nitric acid; thus diglycollic acid (see this) is formed from diethylene alcohol.

2. **Propylene Glycols,** $C_3H_6(OH)_2$.

The two glycols theoretically possible are known. *Trimethylene glycol* [1.3-Propandiol], $CH_2(OH).CH_2.CH_2(OH)$, is formed from trimethylene bromide (B. **16**, 393) and from glycerol in the *schizomycetes-fermentation*, together with n-*butyl alcohol* (B. **20**, R. 706). Moderately oxidized, it forms β-oxypropionic acid or *hydracrylic acid*.

α-**Propylene Glycol** [1.2-Propandiol], $CH_3 . CH(OH) . CH_2 . OH$, is obtained from propylene bromide or chloride. It is most readily prepared by distilling glycerol with sodium hydroxide (B. **13**, 1805). It boils at 188°. At 0° its specific gravity equals 1.051. Platinum black oxidizes it to *ordinary lactic acid*. Only acetic acid is formed when chromic acid is the oxidizing agent. Concentrated hydriodic acid changes it to isopropyl alcohol and its iodide. It contains an asymmetric carbon atom, and when exposed to the action of the ferment *Bacterium termo*, becomes optically active (B. **14**, 843).

3. **Butylene Glycols**, $C_4H_8(OH)_2$.

Five of the six possible butylene glycols are known

Tetramethylene Glycol [1.4-Butandiol], $CH_2(OH) . (CH_2)_2 . CH_2 . OH$, obtained from tetramethylene-dinitramine by means of sulphuric acid, boils at 202–203° (B. **23**, R. 506).

α-**Butylene Glycol**, $CH_3 . CH_2 . CH(OH) . CH_2 . OH$, boils at 191–192°.

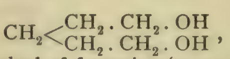
βγ-**Butylene Glycol**, $CH_3 . CH(OH) . CH(OH) . CH_3$, boils at 183–184°.

Isobutylene Glycol, $(CH_3)_2 . C(OH) . CH_2 . OH$, boils at 176–178°.

β-**Butylene Glycol** [1.3-Butandiol], $CH_3 . CH(OH) . CH_2 . CH_2 . OH$, boiling at 207°, is formed by the reduction of *aldol*.

4. **Amylene Glycols**, $C_5H_{10}(OH)_2$.

Pentamethylene Glycol,



$CH_2{<}{\begin{matrix}CH_2 . CH_2 . OH\\ CH_2 . CH_2 . OH\end{matrix}}$, obtained from pentamethylene-diamine by the 4th method of formation (p. 293), boils at 260°.

The following glycols have been made from amylene bromides:

β-**Amylene Glycol**, $CH_3 . CH_2 . CH(OH) . CH(OH) . CH_3$, boils at 187°.

α-**Isoamylene Glycol**, $(CH_3)_2CH . CH(OH) . CH_2(OH)$, boils at 206°.

β-**Isoamylene Glycol**, $(CH_3)_2C(OH) . CH(OH) . CH_3$, boils at 177°.

γ-**Isoamylene Glycol**, $(CH_3)_2C(OH)CH_2 . CH_2OH$, boils at 203° (B. **29**, R. 92).

[2.4-*Pentandiol*], $CH_3CH(OH)CH_2CHOHCH_3$, obtained by the reduction of acetyl-acetone, boils at 177°.

γ-**Pentylene Glycol**, $CH_3 . CH(OH) . CH_2 . CH_2 . CH_2 . OH$, is formed from aceto-propyl alcohol, by reduction. It boils at 219°, and partly decomposes into water and *γ*-pentylene oxide.

Pentaglycol, $(CH_3)_2C(CH_2OH)_2$, melting at 129° and boiling at 110°, is produced by the condensation of isobutyraldehyde and formaldehyde by lime.

5. **Hexylene Glycols**, $C_6H_{12}(OH)_2$.

δ-**Hexylene Glycol**, $CH_3 . CH(OH) . (CH_2)_3 . CH_2OH$, is obtained from aceto-butyl alcohol (see this). It boils at 235° (under 710 mm. pressure) and speedily passes into *δ-hexylene oxide*. **Hexamethylene Glycol**, $HO[CH_2]_6OH$ (B. **27**, 217; R. 735).

Pinacone, Tetramethyl-ethylene Glycol, $(CH_3)_2 . C(OH) . C(OH) . (CH_3)_2 + 6H_2O$, is formed, together with isopropyl alcohol, when sodium (B. **27**, 454) (see 7th method of formation, p. 294) acts upon aqueous acetone. It crystallizes from its aqueous solution in quadratic plates (hence the name, from πίναξ, plate), melting at 42°, and gradually efflorescing on exposure. In the anhydrous state it melts at 38° and boils at 171–172°.

When heated with dilute sulphuric or hydrochloric acid pinacone parts with one molecule of water, and by intramolecular transposition, becomes *pinacoline*, or *tertiary* *butyl-methyl ketone.* Its isomeride, *tetramethyl-ethylene oxide* (p. 299), is also known. It combines readily with water, yielding pinacone.

A series of aliphatic ketones has been prepared by reduction in the same manner as with pinacone: *tetra-alkylized ethylene glycols* have been made. It is customary to designate these as *pinacones.* They behave just like *pinacone* toward dilute sulphuric and hydrochloric acids.

Di-isopropyl Glycol, $[(CH_3)_2CH \,.\, CH \,.\, OH]_2$, melting at 51.5° and boiling at 222–223°, has been prepared from isobutyraldehyde by method 6 (p. 293). Isovaleraldehyde has yielded the corresponding disecondary glycol, and a mixture of isobutyl- and isovaler-aldehyde gave a mixed disecondary glycol. *Methyl-n-propyl-ethyl ethylene glycol*, $CH_3(C_3H_7)C(OH)CH(OH)C_2H_5$ (B. **27**, R. 166).

B. UNSATURATED GLYCOLS, OLEFINE GLYCOLS, ACETYLENE GLYCOLS.

Unsaturated diacid alcohols have been but slightly investigated. The simplest representatives possible theoretically are not known, and probably are not capable of existing.

See p. 299, upon the view of furfurane as an oxide of an unknown, unsaturated glycol. Also consult acetonyl acetone (see this).

Dipropionyl, dibutyryl, and di-isovaleryl are olefine glycol derivatives. They resulted from the action of metallic sodium upon an ethereal solution of propionyl chloride, butyryl chloride, and isobutyryl chloride. They are esters of alkyl acetylene glycols (Klinger and Schmitz, B. **24**, 1271; B. **28**, R. 1000).

Diethyl-acetylene Glycol Dipropionate, Dipropionyl, $\begin{array}{l} C_2H_5 \,.\, CO \,.\, COC_2H_5 \\ C_2H_5 \,.\, \ddot{C}O \,.\, COC_2H_5 \end{array}$, boils at 108° (10 mm.). *Di-n-propylacetylene Glycol Dibutyrate*, Dibutyryl, $\begin{array}{l} C_3H_7 \,.\, C \,.\, CO \,.\, C_3H_7 \\ C_3H_7 \,.\, \ddot{C} \,.\, CO \,.\, C_3H_7 \end{array}$, boils at 119-130° (12 mm.). *Di-isobutyl Acetylene Glycol Di-isovalerate*, Di-isovaleryl, $\begin{array}{l} (CH_3)_2 \,.\, CH \,.\, CH_2 \,.\, C - OCOC_4H_9 \\ (CH_3)_2 \,.\, CH \,.\, CH_2 \,.\, \ddot{C} - O \,.\, COC_4H_9 \end{array}$, boils at 145–155° (12 mm.). Butyroïn and isovaleroïn, the corresponding *a*-ketone alcohols (see this), are produced, and not the alkyl acetylene glycols, when these three compounds are saponified.

Hexa-di-indiol, $CH_2(OH)C \vdots C - C \vdots C \,.\, CH_2 \,.\, OH$, melting at 111°, is a *diacetylene glycol.* It is formed by the oxidation of the precipitate from propargyl alcohol and ammoniacal cupric chloride with potassium ferricyanide (Ch. C. 1897, 1, 281).

GLYCOL DERIVATIVES.

1. ALCOHOL ETHERS OF THE GLYCOLS.

A. The **alcohol-ethers** are obtained from the metallic glycollates by the action of the alkyl iodides.

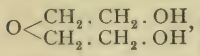
The monoalkyl ethers of the glycols arise also in the union of *ethylene oxide* with alcohol:

$$C_2H_4{<}^{ONa}_{OH} + C_2H_5I = NaI + C_2H_4{<}^{O \,.\, C_2H_5}_{OH}, \text{ Glycol monoethyl ether, b. p. 127°.}$$

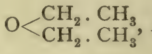
$$C_2H_4{<}^{ONa}_{ONa} + 2C_2H_5I = 2NaI + C_2H_4{<}^{O \,.\, C_2H_5}_{O \,.\, C_2H_5}, \text{ Glycol diethyl ether, b. p. 123°.}$$

Hydriodic acid decomposes the neutral ethers into alkyl iodides and glycols (B. **26**, R. 719). Glycol itself is capable in various ways of forming ethers. See phenol for the phenyl ethers.

The polyethylene alcohols are most closely related to the alcohol ethers. They have been already considered after ethylene glycol (p. 295). Diethylene glycol sustains the same relation to glycol as ethyl ether bears to ethyl alcohol:



$O<\begin{matrix}CH_2.CH_2.OH\\CH_2.CH_2.OH\end{matrix}$, **Diethylene Glycol** (First Ether of Glycol).

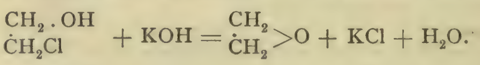


$O<\begin{matrix}CH_2.CH_3\\CH_2.CH_3\end{matrix}$, *Ethyl Ether*.

B. **Cyclic Ethers of the Glycols, Alkylen Oxides.**

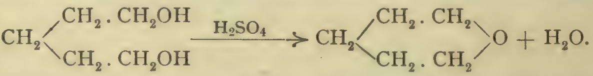
By assuming the exit of a second molecule of water from diethylene glycol, the first ether of glycol, there arises *Diethylene Oxide*, $O<\begin{matrix}CH_2.CH_2\\CH_2.CH_2\end{matrix}>O$, melting at 9° and boiling at 102°; a polymeric ethylene oxide (compare polymeric aldehydes), the second ether of glycol. It is obtained from the red, crystalline brom-addition product of ethylene oxide, $(C_2H_4O)_2Br_2$, melting at 65° and boiling at 95°, when it is treated with mercuric oxide. *Ethylene Methyl Ether*, $\begin{matrix}CH_2.O\\CH_2.O\end{matrix}>CH_2$, boiling at 78°, is obtained from trioxymethylene, ethylene glycol and ferric chloride (B. **28**, R. 109). *Ethylene Ethidene Ether*, $\begin{matrix}CH_2.O\\CH_2.O\end{matrix}>CH.CH_3$, boiling at 82.5°, results from the union of ethylene oxide and acetaldehyde. It is isomeric with diethylene oxide. The latter is a cyclic double ether. But *ethylene oxide*, $\begin{matrix}CH_2\\CH_2\end{matrix}>O$, the third ether of glycol (Würtz), is the simpler cyclic ether of glycol.

The simple cyclic ethers of the glycols, the alkylen oxides, are readily produced in various ways, depending upon whether the two OH-groups are attached to adjacent carbon atoms or not. Alkylen oxides, in which the O-atoms are in union with adjacent carbon atoms, are termed the *a*-alkylen oxides, while the others are the β-, γ-, δ-alkylen oxides. (1) Ethylene oxide itself and the ethylene oxides, as well as the β-alkylen oxides (trimethylene oxide), are prepared by the action of caustic potash upon the *chlor-* or *brom-hydrins*, the monohaloid esters of the respective glycols:



$$\begin{matrix}CH_2.OH\\CH_2Cl\end{matrix} + KOH = \begin{matrix}CH_2\\CH_2\end{matrix}>O + KCl + H_2O.$$

(2) The γ- and δ-alkylen oxides (γ-*pentylene oxide*, *pentamethylene oxide*) are formed when the glycols are heated with sulphuric acid (B. **18**, 3285; **19**, 2843):

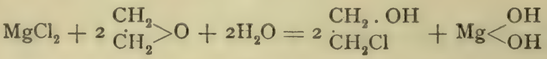


$$CH_2<\begin{matrix}CH_2.CH_2OH\\CH_2.CH_2OH\end{matrix} \xrightarrow{H_2SO_4} CH_2<\begin{matrix}CH_2.CH_2\\CH_2.CH_2\end{matrix}>O + H_2O.$$

The *a*-glycols, under like treatment, lose water and yield either unsaturated alcohols, aldehydes, or pinacolines, depending upon their constitution (p. 214).

The ethylene oxide ring is easily ruptured, hence ethylene oxide enters into addition reactions quite as freely as its isomeride acetaldehyde. The rings of tetra- and pentamethylene oxides, however, are far more stable. These can only be broken up by the haloid acids.

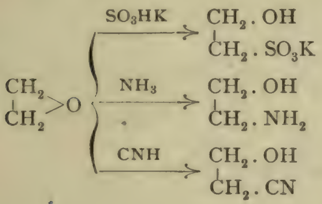
Ethylene Oxide, $\begin{matrix}CH_2\\CH_2\end{matrix}>O$, boiling at 12.5°, sp. gravity 0.898 (0°), isomeric with acetaldehyde, $CH_3.CHO$, is a pleasantly smelling, ethereal, mobile liquid, with a neutral reaction, yet able to gradually precipitate metallic hydroxides from many metallic salts (Magn. Rot. und Refract., see B. **26**, R. 497):



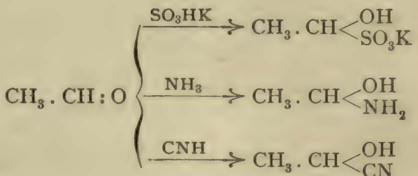
$$MgCl_2 + 2\begin{matrix}CH_2\\CH_2\end{matrix}>O + 2H_2O = 2\begin{matrix}CH_2.OH\\CH_2Cl\end{matrix} + Mg<\begin{matrix}OH\\OH\end{matrix}.$$

Ethylene oxide is characterized by its additive power. (1) It combines with water and slowly yields *glycol.* (2) Nascent hydrogen converts it into ethyl alcohol. (3) The halogen hydrides unite with it to form halohydrins, the monohaloid esters of the glycols. (4, *a*) With alcohol it yields glycol monoethyl ether; (*b*) with glycol it forms diethylene glycol; (*c*) and with the latter it combines to triethylene glycol. (5) It forms ethylene ethidene ether (see above) with aldehyde. (6) Acetic acid and ethylene oxide form glycol monacetate, and (7) with acetic anhydride the product is glycol diacetate. (8) Sodium bisulphite changes it to sodium isethionate. (9) Ammonia changes ethylene oxide to oxethylamine. (10) With hydrocyanic acid it forms the nitrile of *ethylene lactic acid* or *hydracrylic acid*, from which hydrochloric acid produces the ethylene lactic acid itself. Caustic potash polymerizes ethylene oxide at 50–60° (B. **28**, R. 293).

For comparison, the following additive-reactions of ethylene oxide and aldehyde are arranged side by side:



$$\begin{array}{l}CH_2\\|\\CH_2\end{array}\!>O\left\{\begin{array}{l}\xrightarrow{SO_3HK}\begin{array}{l}CH_2\,.\,OH\\|\\CH_2\,.\,SO_3K\end{array}\\ \xrightarrow{NH_3}\begin{array}{l}CH_2\,.\,OH\\|\\CH_2\,.\,NH_2\end{array}\\ \xrightarrow{CNH}\begin{array}{l}CH_2\,.\,OH\\|\\CH_2\,.\,CN\end{array}\end{array}\right.$$



$$CH_3\,.\,CH:O\left\{\begin{array}{l}\xrightarrow{SO_3HK} CH_3\,.\,CH<^{OH}_{SO_3K}\\ \xrightarrow{NH_3} CH_3\,.\,CH<^{OH}_{NH_2}\\ \xrightarrow{CNH} CH_3\,.\,CH<^{OH}_{CN}\end{array}\right.$$

a-Propylene Oxide, $\substack{CH_3CH\\ \cdot \\ CH_2}>O$, boils at 35°, *Isobutylene Oxide,* $\substack{(CH_3)_2C\\ | \\ CH_2}>O$, at 51–52°, sym. *Dimethyl-ethylene Oxide* at 82°; *trimethylethylene oxide* at 75–76°; *tetramethyl-ethylene oxide,* boiling at 95–96°, combines with water, with the evolution of much heat, and yields pinacone (p. 296).

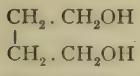
Trimethylene Oxide, $CH_2<^{CH_2}_{CH_2}>O$, boils at 50°. Preparation, p. 205.

Tetramethylene Oxide, Tetrahydro-furfurane, $\substack{CH_2\,.\,CH_2\\ | \\ CH_2\,.\,CH_2}>O$, boils at 57° (B. **25**, R. 912). *γ-Pentylene Oxide,* $\substack{CH_2\,.\,CH(CH_3)\\ | \\ CH_2\,.\,CH_2}>O$, boils at 77° (p. 296; B. **22**, 2571).

Pentamethylene Oxide, $CH_2<^{CH_2\,.\,CH_2}_{CH_2\,.\,CH_2}>O$, boils at 82° (B. **27**, R. 197).

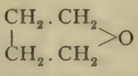
δ-Hexylene Oxide, $CH_2<^{CH_2\,.\,CH(CH_3)}_{CH_2\,.\,CH_2}>O$, boiling at 104°, does not combine with ammonia (B. **18**, 3283).

Addendum.—Furfurane corresponds to tetramethylene oxide. It may be considered as the cyclic ether of an unknown, unsaturated glycol. It is not probable that this glycol could exist; it would be more probable that it would rearrange itself to succindialdehyde, and this in turn to γ-butyrolactone (see this):



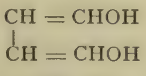
$$\begin{array}{l}CH_2\,.\,CH_2OH\\|\\CH_2\,.\,CH_2OH\end{array}$$

Tetramethylene Glycol



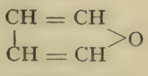
$$\begin{array}{l}CH_2\,.\,CH_2\\|\\CH_2\,.\,CH_2\end{array}\!>O$$

Tetramethylene Oxide



$$\begin{array}{l}CH=CHOH\\|\\CH=CHOH\end{array}$$

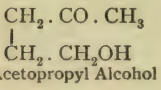
Unknown



$$\begin{array}{l}CH=CH\\|\\CH=CH\end{array}\!>O$$

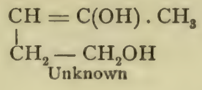
Furfurane.

Acetpropyl alcohol, furthermore, has yielded 1-methyldihydrofurfurane—the alcohol corresponding to it would very probably at once rearrange itself into acetylpropyl alcohol (p. 52):



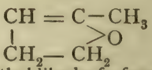
$$\begin{array}{l} CH_2.CO.CH_3 \\ | \\ CH_2.CH_2OH \end{array}$$

Acetopropyl Alcohol



$$\begin{array}{l} CH = C(OH).CH_3 \\ | \\ CH_2 - CH_2OH \end{array}$$

Unknown

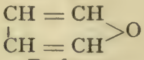


$$\begin{array}{l} CH = C-CH_3 \\ | \qquad\quad >O \\ CH_2 - CH_2 \end{array}$$

1-Methyldihydrofurfurane.

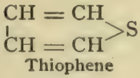
By the substitution of sulphur and again of the NH-group for oxygen in furfurane the products are thiofurfurane, which, from its remarkable resemblance to benzene, has been called **Thiophene, and Pyrrol.**

Notwithstanding that the manner of union in the rings of these heterocyclic compounds is not definitely known, it is possible to refer many bodies to them:



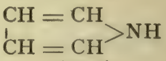
$$\begin{array}{l} CH = CH \\ | \\ CH = CH \end{array}\!>O$$

Furfurane



$$\begin{array}{l} CH = CH \\ | \\ CH = CH \end{array}\!>S$$

Thiophene



$$\begin{array}{l} CH = CH \\ | \\ CH = CH \end{array}\!>NH$$

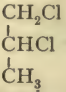
Pyrrol.

All of them contain rings, and they will be discussed later in conjunction with related classes of heterocyclic derivatives.

2. ESTERS OF THE DIHYDRIC ALCOHOLS OR GLYCOLS.

A. Esters of Inorganic Acids.

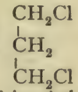
(*a*) **Haloid Esters of the Glycols.**—The glycols and monobasic acids yield neutral and basic esters. The dihalogen substitution products of the paraffins are the neutral or secondary haloid esters of the glycols. The halogen atoms in them are attached to different carbon atoms. They are isomeric with the *aldehyde haloids* (p. 201) and the *ketone haloids* (p. 216), having an equally large carbon content:



$$\begin{array}{l} CH_2Cl \\ | \\ CHCl \\ | \\ CH_3 \end{array}$$

Propylene Chloride

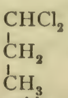
and



$$\begin{array}{l} CH_2Cl \\ | \\ CH_2 \\ | \\ CH_2Cl \end{array}$$

Trimethylene Chloride

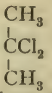
are isomeric with



$$\begin{array}{l} CHCl_2 \\ | \\ CH_2 \\ | \\ CH_3 \end{array}$$

Propidene Chloride (p. 201)

and



$$\begin{array}{l} CH_3 \\ | \\ CCl_2 \\ | \\ CH_3 \end{array}$$

Chloracetol (p. 217).

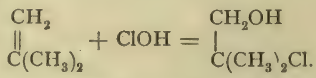
The basic or primary haloid esters of the glycols are the *halohydrins.* These are obtained:

(1) When the glycols are treated with hydrochloric and hydrobromic acids:

$$C_2H_4{<}^{OH}_{OH} + HCl = C_2H_4{<}^{OH}_{Cl} + H_2O.$$

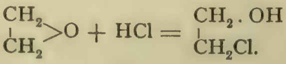
When heated with HI, a more extensive reaction occurs. Ethyl iodide (p. 142) is obtained from ethylene glycol.

(2) They can be obtained, too, by the direct addition of hypochlorous acid to the alkylens (B. 18, 1767, 2287):



$$\begin{array}{l} CH_2 \\ \| \\ C(CH_3)_2 \end{array} + ClOH = \begin{array}{l} CH_2OH \\ | \\ C(CH_3)_2Cl. \end{array}$$

(3) By the action of haloid acids upon ethylene oxide and its homologues:



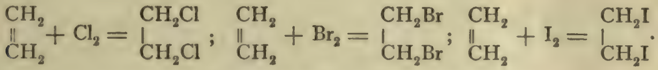
$$\begin{array}{l} CH_2 \\ | \\ CH_2 \end{array}\!>O + HCl = \begin{array}{l} CH_2.OH \\ | \\ CH_2Cl. \end{array}$$

Glycolchlorhydrin, Ethylene chlorhydrin, $CH_2Cl.CH_2OH$, boils at 128°. *Glycolbromhydrin* boils at 147°. *Trimethyleneglycolchlorhydrin*, $CH_2Cl.CH_2.CH_2OH$, boiling at 160°, is obtained by means of HCl from trimethylene glycol. *a-Propylene glycol-a-chlorhydrin*, $CH_3.CH(OH)CH_2Cl$, boiling at 127°, is prepared from allyl chloride by the action of dilute sulphuric acid. *a-Propylene glycol-β-chlorhydrin*, $CH_3.CHCl.CH_2OH$, boiling at 127°, is formed when ClOH adds itself to propylene. *Isobutylene glycol-β-chlorhydrin*, $Cl.C(CH_3)_2.CH_2OH$, boils at 128–130°. *Ethyl chlor-ether*, *β-ethoxy-a-chlorbutane*, boiling at 141°, is formed by the interaction of *a,β-dichlorether* and zinc ethide (B. **28**, 3111).

The primary haloid esters can also be considered as substitution products of the monohydric alcohols. Glycol chlorhydrin would be chlor-ethyl alcohol. (1) Nascent hydrogen converts them into primary alcohols. (2) Oxidizing agents convert them into halogen fatty acids, *e. g.*, glycol chlorhydrin yields *monochloracetic acid;* trimethylene-glycol chlorhydrin yields *β-chlorpropionic acid; a*-propylene glycol-β-chlorhydrin yields *a-chlorpropionic acid*, and isobutylene glycol-β-chlorhydrin yields *a-chlorisobutyric acid.* (3) They change to alkylen oxides under the influence of alkalies. (4) Basic esters of the glycols are produced when they combine with salts of organic acids; *e. g.*, glycol chlorhydrin and potassium acetate yield *glycol monoacetate*, $CH_3.COO.CH_2.CH_2OH$. (5) Potassium cyanide changes them to nitriles of the oxyacids.

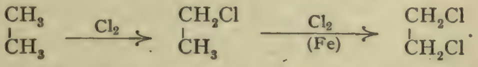
Neutral Haloid Esters of the Glycols are very important starting-points in the preparation of the glycols; compare methods 1 and 4 for the formation of glycols, p. 293.

Methods of Formation.—(1) By the addition of halogens to the olefines—*e. g.*, ethylene—ethylene chloride, bromide and iodide result:



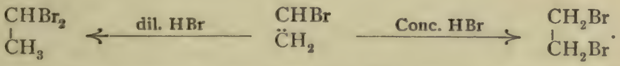
$$\begin{array}{l}CH_2\\ \|\\ CH_2\end{array} + Cl_2 = \begin{array}{l}CH_2Cl\\ |\\ CH_2Cl\end{array};\quad \begin{array}{l}CH_2\\ \|\\ CH_2\end{array} + Br_2 = \begin{array}{l}CH_2Br\\ |\\ CH_2Br\end{array};\quad \begin{array}{l}CH_2\\ \|\\ CH_2\end{array} + I_2 = \begin{array}{l}CH_2I\\ |\\ CH_2I\end{array}.$$

(2) By the substitution of paraffins and monohalogen paraffins:



$$\begin{array}{l}CH_3\\ |\\ CH_3\end{array} \xrightarrow{Cl_2} \begin{array}{l}CH_2Cl\\ |\\ CH_3\end{array} \xrightarrow[(Fe)]{Cl_2} \begin{array}{l}CH_2Cl\\ |\\ CH_2Cl\end{array}.$$

(3) By the addition of halogen hydrides to monohalogen olefines. In this instance much will depend on the temperature, concentration, and other conditions, as to whether both or only one of the two possible isomerides is formed:



$$\begin{array}{l}CHBr_2\\ |\\ CH_3\end{array} \xleftarrow{\text{dil. HBr}} \begin{array}{l}CHBr\\ \|\\ CH_2\end{array} \xrightarrow{\text{Conc. HBr}} \begin{array}{l}CH_2Br\\ |\\ CH_2Br\end{array}.$$

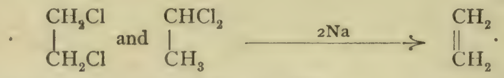
(4) By the action of HCl, HBr or HI upon glycols and glycol chlorhydrins. The second OH will be replaced with more difficulty, and at a higher temperature, than the first.

(5) When PCl_5 acts upon glycols.

(6) From bromides, iodides can be obtained by KI, and chlorides by means of $HgCl_2$.

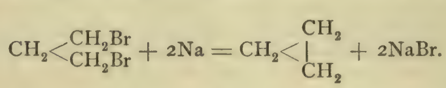
Properties.—The simple dichlor- and dibrom-esters of the glycols, or olefine dichlorides and dibromides, volatilize without decomposition. The di-iodides decompose readily in the light, and when distilled break down into olefines and iodine. The ethylene dihaloids have a very pleasant odor.

Transformations.—(1) The dihalogen paraffins are converted into olefines by sodium:



$$\begin{matrix} CH_2Cl \\ | \\ CH_2Cl \end{matrix} \text{ and } \begin{matrix} CHCl_2 \\ | \\ CH_3 \end{matrix} \xrightarrow{2Na} \begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix}.$$

The production of *trimethylene* from trimethylene bromide and sodium or zinc is noteworthy:



$$CH_2<\begin{matrix} CH_2Br \\ CH_2Br \end{matrix} + 2Na = CH_2<\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix} + 2NaBr.$$

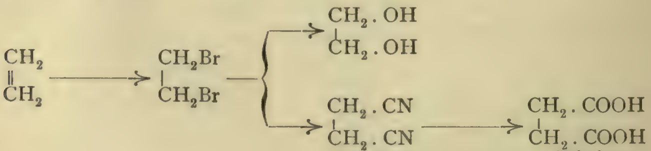
(2) Nascent hydrogen converts both di and mono-halogen paraffins into paraffins. This is the reverse of substitution—*retrogressive substitution* (p. 101).

(3) When digested with alcoholic potash, a halogen hydride splits off, and monohalogen olefines and acetylenes result (p. 95).

(4) Suitable reagents change dihalogen paraffins into the corresponding glycols (p. 293) or their esters.

(5) Ammonia produces alkylen diamines.

(6) Potassium cyanide converts them into the nitriles of monohalogen acids, and the nitriles of dicarboxylic acids. These are classes of bodies whose connection with the glycols is indicated by the dihalogen paraffins:



Ethylene Cyanide

Ethylene Succinic Acid.

Ethylene Haloids—**Ethylene Chloride,** *Elayl Chloride, Oil of the Dutch chemists,* $CH_2Cl \,.\, CH_2Cl$, boiling at 84°, can be prepared (A. **94**, 245) by conducting ethylene into a gently heated mixture of 2 parts of manganese dioxide, 3 parts of salt, 4 parts of water and 5 parts of sulphuric acid. It is insoluble in water, has an agreeable odor, sweet taste, and the sp. gr. 1.2808 (at 4°).

Ethylene Bromide, $CH_2Br \,.\, CH_2Br$, melting at + 9° and boiling at 131°, is formed when ethylene is introduced into bromine, contained in a wide condenser bent at right angles, and covered with a layer of water (A. **168**, 64). It is also produced when ethyl bromide, bromine and iron wire are heated to 100° (B. **24**, 4249).

Ethylene Iodide, $CH_2I \,.\, CH_2I$, melting at 81°, is formed on conducting ethylene into a paste of iodine and ethyl alcohol (J. **1864**, 345).

History of the Alkylen Haloids.—The four Dutch chemists, Deiman, Paets van Troostwyk, Bondt and Lauwerenburgh, while studying the action of chlorine upon ethylene, first obtained ethylene chloride in 1795 as an oil-forming reaction product. Hence they called ethylene "gas huileux," *oily gas*, a name which Fourcroy altered to "gas olefiant," "*oil-forming gas*" (see Roscoe and Schorlemmer, Org. Ch., 1, 647). This phrase subsequently gave the name "*olefines*" to the series. Balard, the discoverer of bromine, obtained ethylene bromide in 1826 on allowing bromine to act upon ethylene (A. chim. phys. [2] 32, 375). Faraday, in 1821, prepared ethylene iodide by acting on ethylene with iodine in sunlight.

Propylene Haloids.—1.2-*Dihalogen propanes*, $CH_3 . CHX . CH_2X$, and **Trimethylene Haloids**, 1.3-*Dihalogen propanes*, $CH_2X . CH_2CH_2X$. The propylene haloids are produced by the addition of the halogens to propylene, and of halogen hydrides to allyl haloids at 100°. Trimethylene bromide results from allyl bromide and hydrogen bromide at —20°. $HgCl_2$ and KI convert the bromide into the chloride and trimethylene iodide.

Propylene chloride,	b. p., 97°;	Trimethylene chloride,	b. p., 119°.
" bromide,	" 141°;	" bromide,	" 165°.
" iodide	decomposes;	" iodide	decomposes.

Higher Homologous Polymethylene Bromides (J. pr. Ch. [2] 39, 542; B. 27, R. 735).

Tetramethylene Bromide, 1.4-Dibrombutane, $CH_2Br[CH_2]_2CH_2Br$, boils at 189°.

Pentamethylene Bromide, 1.5-Dibrompentane, $CH_2Br[CH_2]_3CH_2Br$, boils at 205°.

Hexamethylene Bromide, 1.6-Dibromhexane, $CH_2Br[CH_2]_4CH_2Br$, boils at 243°. Sodium converts these compounds into cycloparaffins, just as sodium and trimethylene bromide yield trimethylene. Sodium malonic esters, sodium acetoacetic esters, and polymethylene bromides produce cycloparaffin carboxylic esters (see these). Mixed, neutral haloid esters of the glycols, containing two different halogen atoms, are also known.

Ethylene Nitrate, $C_2H_4(O . NO_2)_2$, is produced on heating ethylene iodide with silver nitrate in alcoholic solution, or by dissolving glycol in a mixture of concentrated sulphuric and nitric acids:

$$C_2H_4(OH)_2 + 2NO_2 . OH = C_2H_4(O . NO_2)_2 + 2H_2O.$$

This reaction is characteristic of all hydroxyl compounds (the polyhydric alcohols and polyhydric acids); the hydrogen of hydroxyl is replaced by the NO_2 group.

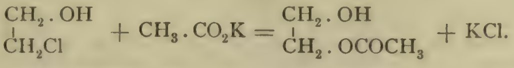
The nitrate is a yellowish liquid, insoluble in water, and has a specific gravity of 1.483 at 8°. It explodes when heated (like the so-called nitroglycerol). The alkalies saponify the esters with formation of nitric acid and glycol.

Glycol or Ethylene-hydroxy-sulphuric Acid, $C_2H_4\!<\!\begin{smallmatrix}OH\\O . SO_2 . OH\end{smallmatrix}$, is produced on heating glycol with sulphuric acid. It is perfectly similar to ethyl sulphuric acid (p. 145), and decomposes, when boiled with water or alkalies, into glycol and sulphuric acid.

B. Esters of Carbonic Acids.

In studying the fatty acids we learned the method of forming esters with monohydric alcohols. The same methods serve for the production of esters of the fatty acids with dihydric alcohols or glycols.

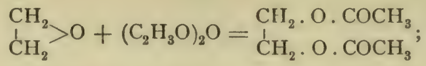
(1) From the haloid esters of the glycols: halohydrins and alkylen haloids with fatty-acid salts:



$$\begin{matrix}CH_2 . OH\\ | \\ CH_2Cl\end{matrix} + CH_3 . CO_2K = \begin{matrix}CH_2 . OH\\ | \\ CH_2 . OCOCH_3\end{matrix} + KCl.$$

(2) From glycols by means of free acids, acid chlorides or acid anhydrides.

(3) There also remains that ester formation resulting from the addition of acids and acid anhydrides to alkylen oxides, just as acid anhydrides add themselves to aldehydes:



$$\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix}\!\!>O + (C_2H_3O)_2O = \begin{matrix} CH_2 . O . COCH_3 \\ | \\ CH_2 . O . COCH_3 \end{matrix};$$

$$CH_3 . CHO + (C_2H_3O)_2O = CH_3 . CH\ (OCOCH_3)_2.$$

Glycol Mono-acetate, $C_2H_4{<}\begin{smallmatrix} O . C_2H_3O \\ OH \end{smallmatrix}$, boils at 182°, and is miscible with water.

If hydrochloric acid gas be conducted into the warmed solution, **glycol chloracetin,** $C_2H_4{<}\begin{smallmatrix} O . C_2H_3O \\ Cl \end{smallmatrix}$, or chlorinated acetic ethyl ester, $CH_2Cl . CH_2 . O . C_2H_3O$, is produced. This boils at 144°.

Glycol Diacetate, $C_2H_4(O . C_2H_3O)_2$, is a liquid of specific gravity 1.128 at 0°, and boiling at 186°. It is soluble in 7 parts of water.

a-Propylene Glycol Diacetate, $CH_3 . C_2H_3(O . COCH_3)_2$, boils at 186°. *Trimethylene Glycol Diacetate,* $(CH_2)_3(OCOCH_3)_2$, boils at 210°.

The formation of the acid esters is well suited for the detection and determination of the number of hydroxyl groups in the polyhydric alcohols, the sugars and the phenols. Benzoic ester particularly is especially easy to prepare. It is only necessary to shake up the substance with benzoyl chloride and sodium hydrate in order to benzoylize all the hydroxyls (B. **21**, 2744; **22**, R. 668, 817). The formation of the *nitric acid ester* is also well adapted for the purpose. See *glycol dinitrate*, p. 303, and also the *carbamic ester* resulting from the action of the isocyanic ester (see this), and especially of the phenyl isocyanic ester (see this).

For carbonic esters of unsaturated glycols, see p. 297.

3. THIOCOMPOUNDS OF ETHYLENE GLYCOL.

Compare the sulphur derivatives of the monohydric alcohols (p. 147), the aldehydes (p. 202), and the ketones (p. 218).

A. Mercaptans.

The mercaptans corresponding to ethylene glycol are formed on treating monochlorhydrin and ethylene bromide with potassium sulphydrate.

The **Monothioethylene Glycol,** $C_2H_4{<}\begin{smallmatrix} SH \\ OH \end{smallmatrix}$, yields isethionic acid (p. 306) when treated with nitric acid.

Dithioglycol Ethylene Thiohydrate, $C_2H_4{<}\begin{smallmatrix} SH \\ SH \end{smallmatrix}$, glycol mercaptan. The odor of this compound is something like that of mercaptan. It boils at 146°; its specific gravity is 1.12. Insoluble in water, it dissolves in alcohol and ether. It shows the reactions of a mercaptan (B. **20**, 461).

B. Sulphides.

(*a*) Alkyl ethers of the Ethylene Mercaptans: *Oxethyl-ethylene Sulphide,* $CH_3 . . CH_2 . S . CH_2 . CH_2OH$, boils at 184°. *Ethylene Dimethyl Sulphide,* $CH_3S . CH_2 . - CH_2SCH_3$, boils at 183°. *Ethylene Diethyl Sulphide* boils at 188°.

(*b*) *Vinylalkyl Ethers of Ethylene Mercaptan* or *Sulphuranes:* **Vinyl-ethyl-ethylene mercaptan,** $CH_2 : CH . S . CH_2 . CH_2 . S . C_2H_5$, boils at 214°. For its formation, see the *sulphine compounds*, which are treated later on.

(*c*) **Thiodiglycol,** $HO . CH_2 . CH_2SCH_2CH_2OH$, corresponding to diglycol, is also known (B. **19**, 3259). However, the simple ethylene sulphide, corresponding to ethylene oxide, is not known, while *Diethylene Oxide Sulphone*, $O<\begin{matrix}CH_2-CH_2\\ CH_2-CH_2\end{matrix}>SO_2$, corresponding to diethylene oxysulphide, and melting at 130°, as well as **Diethylene Disulphide,** are known.

(*d*) *Cyclic Sulphides:* **Diethylene Disulphide,** $S<\begin{matrix}CH_2-CH_2\\ CH_2-CH_2\end{matrix}>S$, melting at 112° and boiling at 200°, is formed from ethylene mercaptan, ethylene bromide, and sodium ethylate. When ethylene bromide is digested with alcoholic sodium sulphide, a polymeric ethylene sulphide, $(C_2H_4S)_n$, melting at 145°, is produced at first. This is a white, amorphous powder, insoluble in the ordinary solvents. Protracted boiling with phenol changes it to diethylene disulphide (A. **240**, 305; B. **19**, 3263; **20**, 2967).

(*e*) *Ethylene Mercaptals* and *Ethylene Mercaptols* are similarly produced from ethylene mercaptan by the action of aldehydes, ketones, and HCl, just as the mercaptals (p. 218) and the mercaptols (p. 204) are obtained from mercaptans (B. **21**, 1473).

Ethylene-dithioethidene, $\begin{array}{l}CH_2S\\ |\\ CH_2S\end{array}>CH\,.\,CH_3$, boils at 173°.

C. **Diethylene Tetrasulphide,** $C_2H_4<\begin{matrix}S_2\\ S_2\end{matrix}>C_2H_4$, is produced by the action of the halogens upon ethylene thiohydrate (or sulphuryl chloride or hydroxylamine. It is a white, amorphous powder, melting at 150° (B. **21**, 1470).

D. **Sulphine Derivatives.**

Ethyl iodide and diethylene disulphide unite to sulphiniodide, $(C_2H_4S)_2C_2H_5I$.

Ethyl Sulphurane, $\begin{array}{l}CH_2\,.\,S\,.\,C_2H_5\\ |\\ CH_2\,.\,S\,.\,C_2H_5\end{array}$, is produced on distilling this iodide with sodium hydroxide. The closed ring of diethylene disulphide is broken.

The union of the derivatives of diethylene disulphide with the higher alkyl iodides yields homologous compounds known as **sulphuranes.** They are the alkyl vinyl ethers of thioethylene (B. **20**, 2967; A. **240**, 305).

E. **Sulphones.**

The disulphones are produced when the open and the cyclic disulphides are oxidized by potassium permanganate. All sulphones, in which sulphone groups are attached to *two adjacent* carbon atoms, can be saponified (Stuffer's law, B. **26**, 1125).

(*a*) *Open Sulphones:* **Ethylene-diethylsulphone,** $\begin{array}{l}CH_2\,.\,SO_2\,.\,C_2H_5\\ |\\ CH_2\,.\,SO_2\,.\,C_2H_5\end{array}$, has been obtained (1) from ethylene dithioethyl; (2) from ethylene bromide by the action of 2 molecules of sodium ethyl sulphinate, and (3) from sodium ethylene disulphinate by the action of 2 molecules of ethyl bromide. The sexivalence of sulphur in the sulphones is thus proved (B. **21**, R. 102). It yields colorless needles, melting at 137°.

(*b*) *Cyclic Sulphones:* **Trimethylene Disulphone,** $\begin{array}{l}CH_2\,.\,SO_2\\ |\\ CH_2\,.\,SO_2\end{array}>CH_2$, melts at 204–205°.

Diethylene Disulphone, $C_2H_4<\begin{matrix}SO_2\\ SO_2\end{matrix}>C_2H_4$ (B. **26**, 1124; **27**, 3043), results from the oxidation of diethylene disulphide.

F. **Sulphone-sulphinic Acids and Disulphinic Acids.**

Oxethylsulphone methylene-sulphinic Acid, $HO\,.\,CH_2\,.\,CH_2\,.\,SO_2\,.\,CH_2\,.\,SO\,.\,OH$, is a syrup-like mass. Its barium salt is formed when trimethylene disulphone is decomposed by baryta water. When the solution is evaporated below 40°, a cyclic ester results, which recalls the lactones, the cyclic esters of the oxycarboxylic acids:

Oxethylsulphomethylene Sulphinic Lactone, $\begin{array}{l}CH_2\,.\,O\,.\,SO_2\\ |\\ CH_2\,.\,O\,.\,SO_2\end{array}>CH_2$, melts at 164° (B.

27, 3043). *Ethylene Disulphinic Acid*, $\begin{array}{l}CH_2.SO.OH\\ |\\ CH_2.SO.OH\end{array}$, is formed by the reduction of ethylene disulphonic acid (p. 307).

G. Sulphonic Acids.

Isethionic Acid, $\begin{array}{l}CH_2.OH\\ |\\ CH_2.SO_3H\end{array}$, *Ethylene Hydrinsulphonic Acid*, *Oxyethylsulphonic Acid*, is isomeric with ethyl sulphuric acid, $SO_4H\cdot(C_2H_5)$, and is produced (1) by oxidizing monothioethylene glycol with HNO_3; (2) by the action of nitrous acid upon taurine or amidoisethionic acid (compare formation of glycollic acid from glycocoll, p. 000):

$$C_2H_4<^{NH_2}_{SO_3H} + NO_2H = C_2H_4<^{OH}_{SO_3H} + N_2 + H_2O;$$

(3) by heating ethylene chlorhydrin with potassium sulphite; (4) by boiling ethionic acid (p. 307) with water; (5) from ethylene oxide and potassium bisulphite.

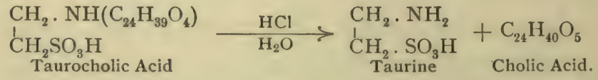
Isethionic acid is a thick liquid, which solidifies when allowed to stand over sulphuric acid. Its salts are very stable and crystallize well.

The *barium salt* is anhydrous. The *ammonium salt* forms plates, which fuse at 135°, and at 210–220° it changes to the ammonium salt of di-isethionic acid, $O(CH_2.CH_2SO_3NH_4)_2$ (B. **14**, 65). *Ethyl isethionate* boils at 120° (see B. **15**, 947). Chromic acid oxidizes the isethionic acid to sulpho-acetic acid.

PCl_5 converts the acid or its salts into the *chloride*, $C_2H_4<^{Cl}_{SO_2.Cl}$, a liquid, boiling at 200°. When it is boiled with water it is converted into chlorethyl-sulphonic acid, $CH_2Cl.CH_2.SO_3H$ (A. **223**, 212).

Taurine, *Amidoisethionic Acid*, *Amidoethyl Sulphonic Acid*, $\begin{array}{l}CH_2NH_2\\ |\\ CH_2.SO_3H\end{array}$, or $\begin{array}{l}CH_2.NH_3\\ |\quad\;\; |\\ CH_2.SO_3\end{array}$ (discovered by Gmelin in 1824; its sulphur content, which had previously been overlooked, was detected in 1846 by Redtenbacher). It is considered in this connection because of its intimate relationship to isethionic and chlorethylene sulphonic acids. It occurs as taurocholic acid, in combination with cholic acid, in the bile of oxen (hence the name—ταῦρος, ox) and many other animals, and also in the different animal secretions.

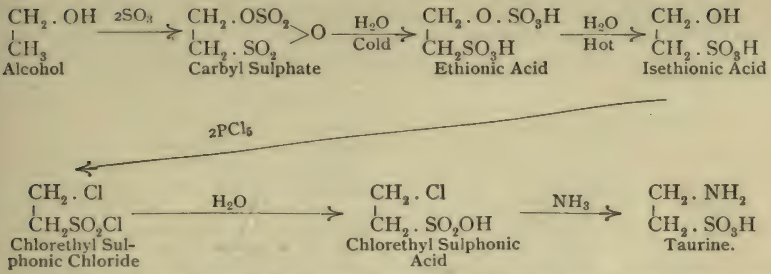
It is formed when taurocholic acid is decomposed with hydrochloric acid:



$$\underset{\text{Taurocholic Acid}}{\begin{array}{l}CH_2.NH(C_{24}H_{39}O_4)\\ |\\ CH_2SO_3H\end{array}} \xrightarrow[H_2O]{HCl} \underset{\text{Taurine}}{\begin{array}{l}CH_2.NH_2\\ |\\ CH_2.SO_3H\end{array}} + \underset{\text{Cholic Acid.}}{C_{24}H_{40}O_5}$$

It can be artificially prepared by heating *chlorethyl sulphonic acid*, $CH_2Cl.CH_2.SO_3H$, with aqueous ammonia (Kolbe, 1862, A. **122**, 33).

This synthesis presupposes that of ethylene or ethyl alcohol (p. 119). Both bodies combine with SO_3 to *carbyl sulphate*, a derivative of isethionic acid. The following diagram shows the course of the synthesis:



$$\underset{\text{Alcohol}}{\begin{matrix}CH_2.OH\\|\\CH_3\end{matrix}} \xrightarrow{2SO_3} \underset{\text{Carbyl Sulphate}}{\begin{matrix}CH_2.OSO_2\\|\\CH_2.SO_2\end{matrix}>O} \xrightarrow[\text{Cold}]{H_2O} \underset{\text{Ethionic Acid}}{\begin{matrix}CH_2.O.SO_3H\\|\\CH_2SO_3H\end{matrix}} \xrightarrow[\text{Hot}]{H_2O} \underset{\text{Isethionic Acid}}{\begin{matrix}CH_2.OH\\|\\CH_2.SO_3H\end{matrix}}$$

$$\xrightarrow{2PCl_5} \underset{\text{Chlorethyl Sulphonic Chloride}}{\begin{matrix}CH_2.Cl\\|\\CH_2SO_2Cl\end{matrix}} \xrightarrow{H_2O} \underset{\text{Chlorethyl Sulphonic Acid}}{\begin{matrix}CH_2.Cl\\|\\CH_2.SO_2OH\end{matrix}} \xrightarrow{NH_3} \underset{\text{Taurine.}}{\begin{matrix}CH_2.NH_2\\|\\CH_2.SO_3H\end{matrix}}$$

Taurine also results when *vinylamine* is evaporated together with sulphurous acid.

Taurine crystallizes in large, monoclinic prisms, insoluble in alcohol, but readily dissolved by hot water. It melts and decomposes about 240°. Taurine contains the groups NH_2 and SO_3H, and is, therefore, both a base and a sulphonic acid. But as the two groups neutralize each other, the compound has a neutral reaction. It may, therefore, be considered as a *cyclic ammonium salt;* this is indicated in the second constitutional formula. It can form salts with the alkalies. It separates unaltered from its solution in acids (see Glycocoll).

Nitrous acid converts it into isethionic acid (p. 306). Boiling alkalies and acids do not affect it, but when fused with caustic potash it breaks up according to the equation :

$$C_2H_4<\genfrac{}{}{0pt}{}{NH_2}{SO_3K} + 2KOH = C_2H_3KO_2 + SO_3K_2 + NH_3 + H_2.$$

Taurine introduced into the animal economy reappears in the urine as *Tauro-carbamic Acid*, $NH_2CONH . CH_2 . CH_2 . SO_3H$.

By introducing methyl into taurine we obtain tauro-betaïne, analogous to betaïne (p. 310): $(CH_3)_3 . \overset{v}{N}<\genfrac{}{}{0pt}{}{C_2H_4}{O}>SO_2$.

Ethionic Acid, $C_2H_4<\genfrac{}{}{0pt}{}{O . SO_3H}{SO_3H}$. The constitution of this acid would indicate it to be both a sulphonic acid and primary sulphuric ester. It is therefore dibasic, and on boiling with water readily yields sulphuric and isethionic acids. It results when carbyl sulphate takes up water.

Carbyl Sulphate, $C_2H_4S_2O_6$ (A. **223**, 210), is formed when the vapors of SO_3 are passed through anhydrous alcohol. It is also produced in the direct union of ethylene with two molecules of SO_3.

Ethylene Disulphonic Acid, $\begin{matrix}CH_2 . SO_3H\\|\\CH_2 . SO_3H\end{matrix}$, is easily soluble in water, melts, when anhydrous, at 94°, and is formed in the oxidation of glycol mercaptan and ethylene sulphocyanide with concentrated nitric acid; by the action of fuming sulphuric acid upon alcohol or ether, and by boiling ethylene bromide with a concentrated solution of potassium sulphite (compare ethylene disulphinic acid, p. 306).

4. NITROGEN DERIVATIVES OF THE GLYCOLS.

A. Nitroso-compounds.

The addition-products from the olefines and nitrosyl chloride belong in this group (compare the terpenes).

Tetramethyl-ethylene-nitrosylchloride, $(CH_3)_2C(NO) . CCl(CH_3)_2$, melting at 121°, has a blue color, and a somewhat penetrating camphor-like odor. The hydrocarbon in hydrochloric-alcoholic solution is mixed, while cooling, with sodium nitrite (B. **27**, 455; R. 467).

B. **Nitro-compounds.**

Only one nitro-derivative of glycol—the primary body—is known.

Nitro-ethyl Alcohol, glycolnitrohydrin, $CH_2(NO_2) . CH_2 . OH$, results from the interaction of glycoliodhydrin and silver nitrite. It is a heavy oil. *Nitro-isopropyl Alcohol*, $CH_3 . CH(OH)CH_2NO_2$, boiling at 112° (30 mm.), sp. gr. 1.191 (18°), is a colorless liquid. It is formed in the condensation of equimolecular quantities of acetaldehyde and nitromethane by means of alkali (B. **28**, R. 606).

1.3-*Dinitropropane*, $NO_2CH_2 . CH_2 . CH_2NO_2$, is the only known secondary nitro-body. It is obtained from trimethylene iodide. All other dinitro-paraffins contain the two nitro-groups joined to the same carbon atom. They are derivatives of the aldehydes or ketones (p. 158).

C. Amines and Ammonium Compounds of the Glycols.

There are two series of amines, derived from the glycols, and corresponding to the two series of glycollates, esters, mercaptans, etc.:

$$\underset{\text{Glycol}}{HO . CH_2 . CH_2 . OH,} \qquad \underset{\text{Oxyethylamine}}{HO . CH_2 . CH_2 . NH_2,} \qquad \text{and} \qquad \underset{\text{Ethylene Diamine.}}{NH_2CH_2 . CH_2 . NH_2}$$

Therefore the amines of the glycols break down into two classes: (1) The oxyalkylamines and their derivatives; (2) the alkylen diamines and their derivatives.

(*a*) **Oxalkyl Bases, or Hydramines** and their derivatives.—Methods of formation: (1) Action of ammonia upon the halohydrins; (2) by the union of ammonia and alkylen oxides. In these two reactions the products are primary, secondary and tertiary oxyalkyl bases, *e. g.:*

$$\begin{array}{l}CH_2\\ |\\ CH_2\end{array}\!>O + NH_3 = \begin{array}{l}CH_2 . OH\\ |\\ CH_2 . NH_2\end{array} \quad \text{Oxyethylamine or Amidoethyl alcohol (p. 124)}$$

$$2\begin{array}{l}CH_2\\ |\\ CH_2\end{array}\!>O + NH_3 = \begin{array}{l}CH_2(OH) . CH_2\\ CH_2(OH) . CH_2\end{array}\!>NH \quad \text{Dioxyethylamine or Imidoethyl Alcohol}$$

$$3\begin{array}{l}CH_2\\ |\\ CH_2\end{array}\!>O + NH_3 = \begin{array}{l}CH_2(OH) . CH_2\diagdown\\ CH_2(OH) . CH_2\!\rightarrow\!N\\ CH_2(OH) . CH_2\diagup\end{array} \quad \text{Trioxyethylamine or Azoethyl Alcohol.}$$

(3) By the action of sulphuric acid upon allylamine with addition of water (B. **16**, 532), or by evaporation with nitric acid, when vinylamine, for example, yields oxethylamine.

(4) By the application of the phthalimide reaction (p. 162). Alkylen haloids are allowed to act upon potassium phthalimide, the reaction-product being heated with sulphuric acid to 200–230°:

$$C_6H_4\left\{\begin{array}{l}O\\ O\end{array}\right.\!>NK \longrightarrow C_6H_4\left\{\begin{array}{l}CO\\ CO\end{array}\right.\!>NCH_2 . CH_2Br \longrightarrow C_6H_4\left\{\begin{array}{l}COOH\\ COOH\end{array}\right. + \begin{array}{l}NH_2CH_2CH_2OH\\ HBr.\end{array}$$

The dialkylic oxyethylamine bases are also called *alkamines;* their carboxylic esters, the *alkeïnes* (see tropeïn) (B. **15**, 1143).

The oxyethylamine bases are separated by fractional crystallization of their HCl-salts, or platinum double salts. They are thick, strongly alkaline liquids, which decompose upon distillation.

Oxy-ethylamine, $CH_2OH . CH_2 . NH_2$, *Amido-ethyl Alcohol* [*2-Aminoethanol*], is produced by the usual methods.

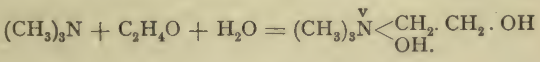
Oxy-ethylmethylamine, $CH_2OH . CH_2 . NH . CH_3$, results from ethylene chlorhydrin and methylamine when they are exposed to a temperature of 110°. It is a liquid, boiling at 130–140°.

Oxy-ethyldimethylamine, $CH_2OH . CH_2 . N(CH_3)_2$, has been obtained from ethylene chlorhydrin and $NH(CH_3)_2$ (B. **14**, 2408); also by the breaking-down of methyl morphimethine (B. **27**, 1144). For homologues and alkamines of cyclic secondary bases, see B. **14**, 1876, 2406; **15**, 1143; **28**, 3111; **29**, 1420.

The bases obtained from the tertiary amines are especially interesting. Choline is one of them. It is quite important physiologically.

Choline, *Oxyethyl-trimethyl Ammonium Hydroxide, Bilineurine, Sincalin,* $C_2H_4<\begin{matrix}OH\\N(CH_3)_3 . OH\end{matrix}$. It is quite widely distributed in the animal organism, especially in the brain, and in the yolk of egg, in which it is present as *lecithin*, a compound of choline with glycerophosphoric acid and fatty acids. It is present in hops, hence occurs in beer. It is obtained, too, from sinapin (the alkaloid of *Sinapis alba*), when it is boiled with alkalies (hence the name *sincalin*). It occurs, together with *muscarine*, $(HO)_2CHCH_2N(CH_3)_3OH$(?) (B. **27**, 166), in fly agaric.

History.—A. Strecker discovered this base (1862) in the bile of swine and oxen. He gave it the name *choline*, from *χολή*, bile. Liebreich obtained it from protagon, a constituent of the nerve substance, and at first named it *neurine*, from *νεῦρον*, nerve; this he later changed to *bilineurine*, to distinguish it from the corresponding vinyl base, which continued to bear the name *neurine*. The constitution of choline was explained by Baeyer, and Würtz showed how it might be synthetically prepared by the action of trimethylamine upon a concentrated aqueous solution of ethylene oxide:



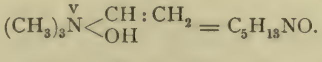
$$(CH_3)_3N + C_2H_4O + H_2O = (CH_3)_3\overset{v}{N}<\begin{matrix}CH_2 . CH_2 . OH\\OH.\end{matrix}$$

Its hydrochloride is produced from ethylene chlorhydrin and trimethylamine.

Choline deliquesces in the air. It possesses a strong alkaline reaction and absorbs CO_2. Its platinum double salt, $(C_5H_{14}ONCl)_2 . PtCl_4$, crystallizes in beautiful reddish-yellow plates, insoluble in alcohol. See B. **27**, R. 738, for choline derivatives.

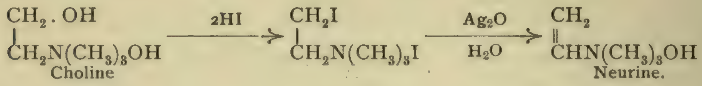
Isocholine, $CH_3 . CH(OH) . N(CH_3)_3 . OH$, is obtained from aldehyde-ammonia (B. 16, 207). **Homocholine,** $HO . CH_2 . CH_2 . CH_2N(CH_3)_3OH$ (B. **22**, 3331).

Neurine, *vinyl-trimethyl-ammonium hydroxide,*



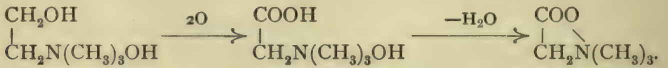
$$(CH_3)_3\overset{v}{N}<\begin{matrix}CH : CH_2\\OH\end{matrix} = C_5H_{13}NO.$$

This base resembles choline. It is very poisonous. It is produced when choline decomposes, or upon boiling it with baryta water. It has also been obtained from the brain substance. It occurs with the *ptomaïnes*—alkaloids of decay, partly poisonous and partly non-toxic. It may be derived from the bromide corresponding to choline (obtained by treating ethylene bromide with trimethylamine), and the iodide (resulting from the action of HI upon choline) when they are subjected to the action of moist silver oxide:



$$\begin{array}{l}CH_2 . OH\\ |\\ CH_2N(CH_3)_3OH\\ \text{Choline}\end{array}\xrightarrow{2HI}\begin{array}{l}CH_2I\\ |\\ CH_2N(CH_3)_3I\end{array}\xrightarrow[H_2O]{Ag_2O}\begin{array}{l}CH_2\\ \|\\ CHN(CH_3)_3OH\\ \text{Neurine.}\end{array}$$

Betaïne, *Oxyneurine, Lycine, Trimethyl glycocoll,* $\begin{array}{l}COO\\ |\quad\diagdown\\ CH_2N(CH_3)_3\end{array}$, is allied to choline. It is obtained by the careful oxidation of choline (Liebreich, B. **2**, 13):



$$\begin{array}{l}CH_2OH\\ |\\ CH_2N(CH_3)_3OH\end{array}\xrightarrow{2O}\begin{array}{l}COOH\\ |\\ CH_2N(CH_3)_3OH\end{array}\xrightarrow{-H_2O}\begin{array}{l}COO\\ |\quad\diagdown\\ CH_2N(CH_3)_3.\end{array}$$

Its hydrochloride is obtained directly by synthesis, when trimethylamine is heated with monochloracetic acid (B. **2**, 167; **3**, 161):

$$(CH_3)_3N + CH_2Cl . CO . OH = (CH_3)_3\overset{v}{N}{<}{}^{CH_2 . CO . OH}_{Cl},$$

and on heating amidoacetic acid (glycocoll), $NH_2 . CH_2 . COOH$, with methyl iodide, caustic potash and wood spirit.

Betaïne occurs already formed in the sugar-beet (Scheibler, B. **2**, 292; **3**, 155), *Beta vulgaris*, hence is present in the molasses from the beet, and makes the latter valuable for the obtainment of trimethylamine. It is also found in the leaves and stalks of *Lycium barbarum*, in cottonseed, and in malt and wheat sprouts (B. **26**, 2151). It crystallizes with one molecule of water in deliquescent crystals, in which there is present the acid $HO . N(CH_3)_3 . CH_2 . CO_2H$. At 100° this ammonium hydroxide loses one molecule of water, and the cyclic ammonium salt, $\begin{array}{l}COO\\ |\quad\diagdown\\ CH_2N(CH_3)_3\end{array}$, is produced.

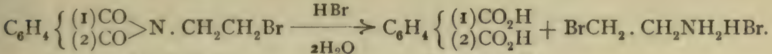
Diethyleneimide Oxide, *Morpholine,* $O{<}{}^{CH_2 . CH_2}_{CH_2 . CH_2}{>}NH$, is produced when dioxyethylamine is heated to 160° with hydrochloric acid, and upon distillation with caustic potash. See B. **22**, 2081, for homologous morpholines. It is assumed that the same atomic grouping exists in morphine as in morpholine, hence the name.

Diacetone Alkamine, $(CH_3)_2C(NH_2)CH_2 . CH . OH . CH_3$, boiling at 174–175°, is formed in the reduction of *diacetonamine* (p. 219) (A. **183**, 290).

(*b*) **Halogen Alkylamines, or Haloid Esters of the Oxyalkylamines.**—In the free state these bodies are soluble in water and not very stable. They easily change to salts of the cyclic imides, *e. g.*, chloramylamine, $ClCH_2(CH_2)_4NH_2$, become pentamethyleneimide- or piperidine chlorhydrate, $\overline{CH_2 . (CH_2)_4 NH} . HCl$. *Methods of Formation:* (1) The addition of a halogen hydride to unsaturated amines, like vinyl- or allylamine, p. 169 (B. **21**, 1055; **24**, 2627, 3220).

(2) By the action of halogen hydrides upon oxyalkylamines, see *neurine*, p. 309;

(3) when the halogen alkyl phthalimides are heated with haloid acids (B. **21**, 2665; **22**, 2220; **23**, 90), *e.g.*:



$$C_6H_4\left\{\begin{matrix}(1)CO\\(2)CO\end{matrix}\right\rangle N.CH_2CH_2Br \xrightarrow[2H_2O]{HBr} C_6H_4\left\{\begin{matrix}(1)CO_2H\\(2)CO_2H\end{matrix}\right. + BrCH_2.CH_2NH_2HBr.$$

Bromethyl-phthalimide o-Phthalic Acid.

(4) Or the nitriles of the halogen substituted acids are transposed with sodium phenoxide, reduced, and then heated with an haloid acid (B. **24**, 3231; **25**, 415):

$$ClCH_2.CH_2CH_2CN + NaOC_6H_5 = C_6H_5O.CH_2.CH_2.CH_2CN + NaCl$$

$$C_6H_5OCH_2[CH]_2CN \xrightarrow{4H} C_6H_5OCH_2[CH_2]_2CH_2NH_2 \xrightarrow{2HCl} ClCH_2[CH_2]_3NH_2.HCl.$$

The following are known:

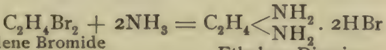
Chlor-, *brom-*, and *iodoethylamine*, $ICH_2.CH_2NH_2$; *γ-Brompropylamine*, $Br.CH_2.CH_2.CH_2NH_2$; *β-Brombutylamine*, $CH_3CH_2CHBrCH_2NH_2$; *γ-Chlorbutylamine*, $CH_3.CHCl.CH_2.CH_2NH_2$ (B. **28**, 3111); *δ-Chlorbutylamine*, $ClCH_2[CH_2]_3NH_2$; *ε-Chloramylamine*, $ClCH_2(CH_2)_4NH_2$; *β-Methyl-ε-chlor-n-amylamine*, $CH_2Cl[CH_2]_2CH(CH_3)CH_2NH_2$; *β-n-Propyl-ε-chlor-n-amylamine*, $CH_2Cl[CH_2]_2CH(C_3H_7)CH_2NH_2$ (B. **27**, 3509; **28**, 1197). The four last bodies split off hydrochloric acid and yield tetramethylene and pentamethylene imides (p. 314), or piperidine, β-pipecoline and β-propylpiperidine.

(*c*) **Oxyethylamine Derivatives Containing Sulphur.**—*Aminoethyl mercaptan chlorhydrate*, $HCl.NH_2.CH_2.CH_2SH$, melts at 70–72°. *Thioethylamine*, $(NH_2.CH_2.CH_2)_2S$, boils at 231–233°. *Diaminoethyl disulphide chlorhydrate*, $(NH_2.CH_2.CH_2S)_2 2HCl$, melts at 253°. *Diaminoethylsulphone*, $(NH_2CH_2CH_2)_2SO_2$, has been prepared from bromethylphthalimide as the starting-out substance (B. **22**, 1138; **24**, 1112, 2132, 3101).

Taurine, *Amidoisethionic Acid,* $NH_2.CH_2.CH_2.SO_3H$, has already been discussed under isethionic acid (p. 306).

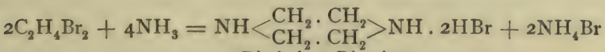
(*d*) **Alkylen Diamines.**—The di-, like the mono-valent alkyls, can replace two hydrogen atoms in two ammonia molecules and produce primary, secondary, and tertiary *diamines*. These are di-acid bases, and are capable of forming salts by direct union with two equivalents of acids. Some of them have been detected with the *ptomaïnes* or alkaloids of decay (B. **20**, R. 68) and are therefore worthy of note, *e.g.*, tetramethylene diamine or *putrescine*, and pentamethylene diamine or *cadaverine*.

Formation: (1) They are prepared by heating the alkylen bromides with alcoholic ammonia to 100° (p. 161) in sealed tubes:



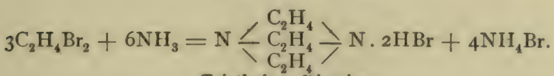
$$C_2H_4Br_2 + 2NH_3 = C_2H_4<\begin{matrix}NH_2\\NH_2\end{matrix}.2HBr$$

Ethylene Bromide Ethylene Diamine



$$2C_2H_4Br_2 + 4NH_3 = NH<\begin{matrix}CH_2.CH_2\\CH_2.CH_2\end{matrix}>NH.2HBr + 2NH_4Br$$

Diethylene Diamine



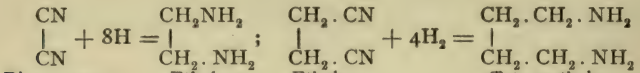
$$3C_2H_4Br_2 + 6NH_3 = N\begin{matrix}\diagup C_2H_4 \diagdown\\ - C_2H_4 - \\ \diagdown C_2H_4 \diagup\end{matrix}N.2HBr + 4NH_4Br.$$

Triethylene Diamine.

To liberate the diamines, the mixture of their HBr-salts is distilled with KOH and the product then fractionated.

(2) Another very convenient method for the preparation of diamines is the reduc-

tion of (*a*) alkylen dicyanides or nitriles (see these) with metallic sodium and absolute alcohol (see p. 162 and B. **20**, 2215):



$$\begin{array}{l}CN\\ |\\ CN\end{array} + 8H = \begin{array}{l}CH_2NH_2\\ |\\ CH_2.NH_2\end{array};\quad \begin{array}{l}CH_2.CN\\ |\\ CH_2.CN\end{array} + 4H_2 = \begin{array}{l}CH_2.CH_2.NH_2\\ |\\ CH_2.CH_2.NH_2\end{array}$$

Dicyanogen Ethylene Diamine Ethylene Cyanide Tetramethylene Diamine.

(*b*) By the reduction of the oximes, (*c*) reduction of the hydrazones of the dialdehydes and diketones, and (*d*) by the reduction of the dinitroparaffins.

In some of these reductions cyclic imides have been observed; thus, in the reduction of ethylene cyanide in the presence of tetramethylene diamine, tetramethylene imide is formed.

(3) From dicarboxylic amides, bromine and caustic potash (B. **27**, **511**) (p. 163).

(4) From dicarboxylic azides; see hexamethylene diamine, p. 313.

(5) From alkylene diphthalimides on heating with HCl:

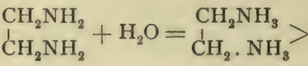
$$C_6H_4\left\{\begin{array}{l}(1)CO\\ (2)CO\end{array}\right>N(CH_2)_3N<\left.\begin{array}{l}CO(1)\\ CO(2)\end{array}\right\}C_6H_4 \xrightarrow[4H_2O]{2HCl} \begin{array}{l}2C_6H_4(CO_2H)_2\\ HCl.NH_2.CH_2.CH_2.CH_2NH_2HCl\end{array}$$

Trimethylene Diphthalimide Trimethylenediamine Chlorhydrate.

Properties.—The alkylen diamines are liquids or low melting solids of peculiar odor, which in the case of those that are volatile is very much like that of ammonia, and recalls piperidine. They fume slightly in the air, and attract carbonic acid.

Behavior.—Alcohol and acid radicals can be introduced into the amido-groups of the diamines in the same manner as in the amido-groups of the monamines. The production of the dibenzoyl derivatives, *e. g.*, $C_2H_4(NH\ CO.C_6H_5)_2$, upon shaking with benzoyl chloride and caustic soda, is well adapted for the detection of the diamines (B. **21**, 2744). Nitrous acid converts them into glycols, at the same time unsaturated alcohols and unsaturated hydrocarbons arise (B. **27**, R. 197)

Further, the diamines unite directly with water, forming very stable *ammonium oxides*, which only give up water again when they are distilled over caustic potash (compare pentamethylene diamine):



$$\begin{array}{l}CH_2NH_2\\ |\\ CH_2NH_2\end{array} + H_2O = \begin{array}{l}CH_2NH_3\\ |\\ CH_2.NH_3\end{array}\!\!>O$$

, Ethylene diamine hydrate.

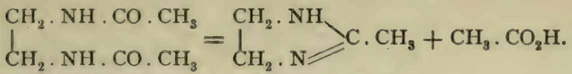
By the exit of ammonia they pass into cyclic imides.

Ethylene Diamine, $C_2H_4<^{NH_2}_{NH_2}$, melting at +8.5°, boiling at 116.5°, combines with water to *ethylene diamine hydrate*, melting at +10° and boiling at 118°. It reacts strongly alkaline, and has an ammoniacal odor.

Nitrous acid converts it into ethylene oxide. *Ethylene Dinitramine*, $NO_2NHCH_2.CH_2NHNO_2$ (B. **22**, R. 295).

Ethylene diamine and $a\beta$-propylene diamine, like the ortho-diamines of the benzene series, combine with ortho-diketones, *e. g.*, phenanthraquinone and benzil, to form pyrazine derivatives, similar in structure to the quinoxalines. They also unite with the benzaldehydes and benzoketones (B. **20**, 276; **21**, 2358). Consult B. **27**, 1663. for the action of $CSCl_2$ upon ethylene diamine.

Diacetyl-ethylene Diamine consists of colorless needles, melting at 172°, When this compound is heated beyond its melting point, water splits off, and there follows an inner condensation that leads to the formation of a cyclic *amidine base*, closely allied to the *glyoxalines*. It is *ethyl-ethenyl amidine* or *methyl glyoxalidine*, which under the name *Lysidine*, m. p. 105° and b. p. 223°, has been recommended as a solvent for uric acid (B. **28**, 1176). The corresponding propylene- and trimethylene-diamine derivatives react similarly:



$$\begin{array}{l} CH_2 . NH . CO . CH_3 \\ | \\ CH_2 . NH . CO . CH_3 \end{array} = \begin{array}{l} CH_2 . NH \\ | \\ CH_2 . N \end{array} \!\!\!\gt C . CH_3 + CH_3 . CO_2H.$$

Diacetyl-diethylene Diamine

Ethylene-ethenyl Amidine.

Propylene Diamine, $\begin{array}{l} CH_3 . CH . NH_2 \\ \quad\;\; | \\ \quad\; CH_2 . NH_2 \end{array}$, boiling at 119–120° (B. **21**, 2359), has been split up by means of d-tartaric acid.

l-**Propylene Diamine,** $[\alpha]_D = -19.11°$, forms a d-tartrate, which is sparingly soluble (B. **28**, 1180).

Trimethylene Diamine, $CH_2<\begin{array}{l} CH_2 . NH_2 \\ CH_2 . NH_2 \end{array}$, boils at 135–136° (B. **17**, 1799; **21**, 2670). It has been prepared by general methods 1 and 3; also (2d) by reduction of 1.3-dinitro-propane (p. 159).

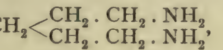
Tetramethylene Diamine, [1.4-*Diaminobutane*], *Putrescine*, $C_4H_8(NH_2)_2$, melting at 27°, is obtained from ethylene cyanide by general method 2*a*, and from succinaldehyde dioxime (p. 327) (B. **22**, 1970). It is identical with the *putrescine* (B. **21**, 2938), which has been isolated from decaying matter.

[**1.4-Diaminopentane**], $CH_3CH(NH_2) . CH_2 . CH_2 . CH_2 . NH_2$, boiling at 172°, is formed from the nitrile of pyroracemic acid according to method of formation 2*a*.

ϕ- and χ-[**2.5-Diaminohexane**], $CH_3CH(NH_2)CH_2 . CH_2CH(NH_2)CH_3$, boiling at 175°, are formed together from the diphenyl-hydrazone of acetonyl acetone (p. 324) according to method of formation 2*c*. They sustain a relation to each other similar to that shown by racemic acid and mesotartaric acid (B. **28**, 379).

[**1.4-Diamino-2-Methyl Pentane**], $CH_3CH(NH_2)CH_2 . CH(CH_3)CH_2NH_2$, boiling at 175°, is obtained from *a* methyl-levulindialdoxime (p. 298) according to method of formation 2*b* (B. **23**, 1790).

Pentamethylene Diamine, *Cadaverine*, [1.5-*Diaminopentane*],



$$CH_2<\begin{array}{l} CH_2 . CH_2 . NH_2 \\ CH_2 . CH_2 . NH_2 \end{array},$$

is obtained by the reduction of trimethylene cyanide by method of formation 2*a*. It boils at 178–179°, and solidifies in the cold (B. **18**, 2956; **19**, 780). It is identical with *cadaverine* (p. 311), a ptomaine isolated from decaying corpses (B. **20**, 2216, and R. 69). It forms an hydrate with two molecules of water (B. **27**, R. 580).

Neuridine, $C_5H_{14}N_2$ (B. **18**, 86), formed by the decay of fish and meat, is isomeric with pentamethylene diamine.

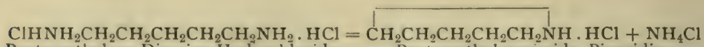
Hexamethylene Diamine, [1.6-*Diaminohexane*], $NH_2[CH_2]_6NH_2$, melting at 40° and boiling at 192–195°, is formed in the decomposition of *Hexamethylene diethyl methane*, $[CH_2]_6[NHCO_2C_2H_5]_2$, melting at 84°, which results upon boiling the suberic acid azide with alcohol (B. **29**, 1169).

[**1.8-Diamino-octane**], $CH_2NH_2[CH_2]_6CH_2NH_2$, melting at 51° and boiling at 238°, is obtained from the amide of sebacic acid by method of formation 3.

1.10-Dekamethylene Diamine, $NH_2CH_2(CH_2)_8CH_2 . NH_2$, melting at 61.5° and boiling at 140° (12 mm.), results from the nitrile of sebacic acid by 2*a* method of formation (B. **25**, 2253).

3. **Cyclic Alkylen Imides.**—Three members of this class are especially important: (1) *Diethylene diamine*, *piperazine* or *hexahydropyrazine;* (2) *Tetramethylene Imide* or *Tetrahydropyrrol;* and (3) *Pentamethylene Imide*, *Hexahydropyridine*, or *Piperidine*, the basic decomposition product of *piperine*, the alkaloid contained in pepper.

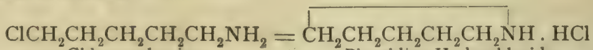
Methods of Formation.—(1) Upon heating the diamine hydrochlorides, when ammonia splits off as ammonium chloride, *e.g.*:



$$ClHNH_2CH_2CH_2CH_2CH_2CH_2NH_2.HCl = \overline{CH_2CH_2CH_2CH_2CH_2NH}.HCl + NH_4Cl$$

Pentamethylene Diamine Hydrochloride — Pentamethylene-imide, Piperidine.

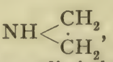
(2) By the splitting-off of halogen hydride from the halogen alkyl amines—*e.g.*, when the chlorhydrate is heated, or when it is digested with dilute caustic potash (B. **24**, 3231; **25**, 415):

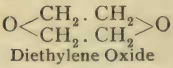


$$ClCH_2CH_2CH_2CH_2CH_2NH_2 = \overline{CH_2CH_2CH_2CH_2CH_2NH}.HCl$$

ε-Chloramylamine — Piperidine Hydrochloride.

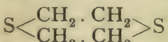
(3) They are produced, together with the diamines, in the reduction of alkylen dicyanides.

The simplest cyclic alkylenimide, ethylene imide,  $NH<\begin{array}{l}CH_2\\ \vdots\\ CH_2\end{array}$, corresponding to ethylene oxide, is not known. However, *piperazine*, a diethylene diamide, corresponding to diethylene oxide (p. 305), diethylene disulphide (p. 299), and diethylene-imide oxide or morpholine, is known:



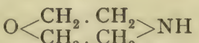
$$O<\begin{array}{l}CH_2.CH_2\\CH_2.CH_2\end{array}>O$$

Diethylene Oxide



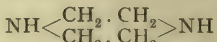
$$S<\begin{array}{l}CH_2.CH_2\\CH_2.CH_2\end{array}>S$$

Diethylene Disulphide



$$O<\begin{array}{l}CH_2.CH_2\\CH_2.CH_2\end{array}>NH$$

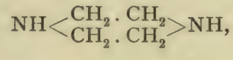
Diethylene-imide Oxide Morpholine



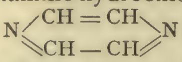
$$NH<\begin{array}{l}CH_2.CH_2\\CH_2.CH_2\end{array}>NH$$

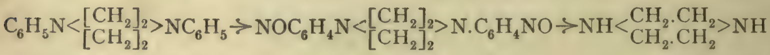
Diethylene-diamine Piperazine.

Diethylene Diamine, *Piperazine, Hexahydropyrazine,*



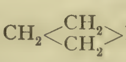
$$NH<\begin{array}{l}CH_2.CH_2\\CH_2.CH_2\end{array}>NH,$$

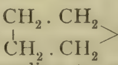
melting at 104° and boiling at 145–146°, was first prepared by the action of ammonia upon ethylene chloride. It is produced by heating ethylene-diamine hydrochloride (B. **21**, 758), and by the reduction of *pyrazine*,  $N\begin{array}{l}\diagup CH=CH\diagdown\\ \diagdown CH-CH\diagup\end{array}N$ (B. **26**, 724). It is technically made from *diphenyl diethylene diamine*, the reaction-product of aniline and ethylene bromide, when it is transposed into the p-dinitroso-compound, and the latter then broken down into p-dinitrosophenol and diethylene diamine:

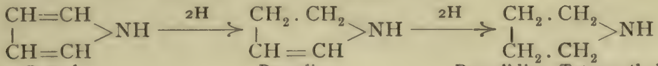


$$C_6H_5N<\begin{array}{l}[CH_2]_2\\ [CH_2]_2\end{array}>NC_6H_5 \rightarrow NOC_6H_4N<\begin{array}{l}[CH_2]_2\\ [CH_2]_2\end{array}>N.C_6H_4NO \rightarrow NH<\begin{array}{l}CH_2.CH_2\\CH_2.CH_2\end{array}>NH$$

Diethylene diamine, or piperazine, is a strong base, soluble in water, which upon distillation with zinc dust, changes to *pyrazine* (see this) (B. **26**, R. 441). It is interesting to note that piperazine unites with uric acid to form a salt even more readily soluble than the lithium salt. Hence its strongly alkaline, dilute solution has been recommended as a solvent for uric acid (B. **24**, 241).

Trimethylene Imide,  $CH_2<\begin{array}{l}CH_2\\CH_2\end{array}>NH$, boils from 66–70° (B. **23**, 2727).

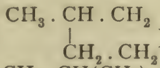
Tetramethylene Imide, *Tetrahydropyrrol, Pyrrolidine,*  $\begin{array}{l}CH_2.CH_2\\ |\\ CH_2.CH_2\end{array}>NH$, boiling at 87°, is obtained from tetramethylene diamine according to method of formation 1; from δ-chlorbutylamine and caustic potash by method 2 (B. **24**, 3231), and by the reduction of pyrroline, the first reaction-product of pyrrol (B. **18**, 2079), and of *succinimide* (see succinic acid) (B. **20**, 2215):

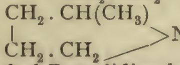


$$\begin{matrix}CH{=}CH \\ | \\ CH{=}CH\end{matrix}{>}NH \xrightarrow{2H} \begin{matrix}CH_2 . CH_2 \\ | \\ CH = CH\end{matrix}{>}NH \xrightarrow{2H} \begin{matrix}CH_2 . CH_2 \\ | \\ CH_2 . CH_2\end{matrix}{>}NH$$

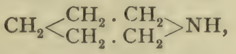
Pyrrol Pyrroline Pyrrolidine, Tetramethylene Imide.

Tetramethylene imide has an odor resembling that of piperidine. *Tetramethylene-nitrosamine*, C_4H_8NNO, boils at 214° (B. **21**, 290).

β-**Methyl Pyrrolidine,**  $\begin{matrix}CH_3 . CH . CH_2 \\ | \\ CH_2 . CH_2\end{matrix}{>}N$, boils at 103° (B. **20**, 1654).

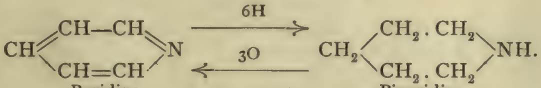
α-**Methyl Pyrrolidine,**  $\begin{matrix}CH_2 . CH(CH_3) \\ | \\ CH_2 . CH_2\end{matrix}{>}NH$, is obtained from *γ*-valerolactam. It boils at 97°. **1.4-Dimethyl Pyrrolidine** boils at 107° (B. **22**, 1859).

Pentamethylene Imide, *Piperidine, Hexahydropyridine,*



$$CH_2{<}\begin{matrix}CH_2 . CH_2 \\ CH_2 . CH_2\end{matrix}{>}NH,$$

boiling at 106°, is obtained according to methods 1, 2 (B. **25**, 415) and 3 (p. 314); also from piperine (see this), and by the reduction of pyridine, into which it passes when it is oxidized:



Pyridine Piperidine.

Piperidine bears the same relation to pyridine that is sustained by pyrrolidine to pyrrol. Therefore, tetramethylene imide and pentamethylene imide link the pyrrol and pyridine groups to the simple aliphatic substances, the diamines, and their parent bodies, the glycols.

The pyrrol and pyridine derivatives will be discussed later in connection with the heterocyclic ring systems, together with allied bodies, and then we shall again return to pyrrolidine and piperidine.

2. ALDEHYDE ALCOHOLS.

These contain both an alcoholic hydroxyl group and the aldehyde group CHO, hence their properties are both those of alcohols and aldehydes (p. 189). The addition of 2 H-atoms changes them to glycols, while by oxidation they yield the oxy-acids, containing a like number of carbon atoms.

(1) **Glycolyl Aldehyde,** $CH_2(OH) . CHO$, may be considered the first aldehyde of glycol, and glyoxal (p. 320) the second or dialdehyde. It is produced when brom-acetaldehyde is treated with cold baryta water, or when chloracetal is heated with very dilute acids; probably also from dioxymaleic acid (?), an oxidation product of tartaric acid, when it is digested with water at 50-60° (B. **29**, R. 919). It is only known in aqueous solution. Bromine water oxidizes it to *glycollic acid* (see this), and dilute caustic soda condenses it to *tetrose* (see this) (B. **25**, 2552, 2984); see aldol. Phenylhydrazine acetate produces the osazone of glyoxal (p. 328).

The following bodies, which have been already discussed, are derivatives of glycol aldehyde:

CHO $\vert$ $CH_2Cl(BrI)$,	$CH(OC_2H_5)_2$ $\vert$ $CH_2Cl(Br)$	$CHCl_2$ $\vert$ CH_2OH	$CHCl_2$ $\vert$ CH_2Cl
Monochlor- (brom-, iodo-) Acetaldehyde (p. 198)	Monochlor-acetal (p. 200)	Dichlorethyl Alcohol (p. 125)	1.2-Trichlor-ethane (p. 103).

Glycol Acetal, $CH_2OH . CH (O . C_2H_5)_2$, boiling at 167°, is obtained from brom-acetal (B. **5**, 150).

Ethyl Glycol Acetal, $C_2H_5O . CH_2 . CH(O . C_2H_5)_2$, boils at 168° and is obtained from 1.2-dichlorether (p. 135) (B. **5**, 150). *Phenyl Glycol Acetal*, $C_6H_5O . CH_2 . CH(O . C_2H_5)_2$, boils at 257° (B. **28**, R. 295). *Isotriethylin*, $CH_3 . CH(OC_2H_5) . CH(O . C_2H_5)_2$, boiling at 85° (11 mm.), is formed when acrolein is digested several days with alcohol at 50° (B. **24**, R. 89), and by the action of orthoformic ether upon acroleïn (B. **29**, 2933).

(2) **Aldol**, $CH_3 . CH(OH) . CH_2 . CHO$, *β-Oxybutyraldehyde*, boiling at 60–70° (12 mm.), and discovered by Würtz in 1872, is obtained by the condensation of acetaldehyde by means of dilute cold hydrochloric acid, and other condensation agents, *e. g.*, CO_3K_2 (B. **14**, 2069; **24**, R. 89; **25**, R. 732).

Aldol freshly prepared is a colorless, odorless liquid, with a specific gravity of 1.120 at 0°, and is miscible with water. Aldol distils in a vacuum undecomposed at 100°; but under atmospheric pressure it loses water and becomes *crotonaldehyde*.

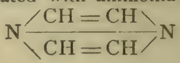
As an aldehyde it will reduce an ammoniacal silver nitrate solution. Heated with silver oxide and water it yields β-oxybutyric acid, $CH_3 . CH(OH) . CH_2 . CO_2H$.

On standing it polymerizes into *paraldol*, $(C_4H_8O_2)_n$, which melts at 80–90°. Should the mixture of aldehyde and hydrochloric acid used for the preparation of aldol stand for some time, water separates, and we obtain the so-called *dialdan*, $C_8H_{14}O_3$. This is a crystalline body which melts at 139° and reduces ammoniacal silver solutions.

NITROGEN-CONTAINING DERIVATIVES OF THE ALDEHYDE ALCOHOLS.

Ammonia converts aldol in ethereal solution into aldol-ammonia, $C_4H_8O_2 . NH_3$, a thick syrup, soluble in water. When heated with ammonia we get the bases, $C_8H_{15}NO_2$, $C_8H_{13}NO$ (oxytetraldin, see this) and $C_8H_{11}N$ (collidine). With aniline aldol forms *methyl quinoline*. (Compare alkylide anilines.)

Amidoaldehydes: (1) **Amidoacetaldehyde**, [*Ethanalamine*], [*2-Amino-ethanal*], $NH_2 . CH_2 . CHO$. This is obtained as a deliquescent hydrochloride when *amido-acetal*, $NH_2 . CH_2(O . C_2H_5)_2$, boiling at 163°, is treated with cold, concentrated hydrochloric acid. Amido-acetal is produced when chloracetal is treated with ammonia (B. **25**, 2355; **27**, 3093). Amidoacetaldehyde yields *pyrazine*,



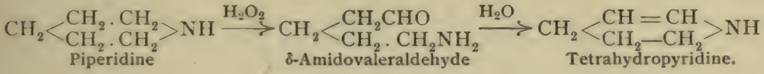
(B. **26**, 1830, 2207), when it is oxidized with sublimate.

Hydrazide Acetaldehyde (B. **27**, 2203).

Betaïne Aldehyde, $(CH_3)_3N . CH_2 . CHO . OH$ (?) (B. **27**, 165), is different from *Muscarine* (p. 309), which occurs in fly agaric (*Agaricus muscarius*).

Isomuscarine, $HO . CH_2 . CH(OH)N(CH_3)_3CH$ (?), is obtained from the addition product of ClOH and neurine (p. 309) with silver oxide (A. **267**, 253, 291).

δ-**Amidovaleraldehyde**, $NH_2 . CH_2 . CH_2 . CH_2 . CH_2 . CHO$, melting at 39°, is obtained from *piperidine* by the action of H_2O_2, and condenses to tetrahydropyridine (B. **25**, 2781) when it is heated. Homologous amidoaldehydes are obtained from conine, *a*- and *β*-pipecoline, as well as copellidine, when treated with hydrogen peroxide (B. **28**, 2273):



$$CH_2<\begin{matrix}CH_2 . CH_2\\CH_2 . CH_2\end{matrix}>NH \xrightarrow{H_2O_2} CH_2<\begin{matrix}CH_2CHO\\CH_2 . CH_2NH_2\end{matrix} \xrightarrow{H_2O} CH_2<\begin{matrix}CH=CH\\CH_2-CH_2\end{matrix}>NH$$

Piperidine δ-Amidovaleraldehyde Tetrahydropyridine.

3. KETONE ALCOHOLS OR KETOLS.

The ketone alcohols or ketols are distinguished, according to the position of the alcohol or ketone groups, as *a*- or 1.2-, *β*- or 1.3-, *γ*- or 1.4-ketols, etc. The position of these two groups with reference to each other influences the chemical character of these bodies more than the kind of alcohol group (whether primary, secondary, or tertiary). These alcohols show simultaneously the character of alcohols and of ketones.

A. SATURATED KETOLS.

a- or **1.2-Ketols** yield, with phenylhydrazine, osazones of 1.2-aldehyde ketones or 1.2-diketones (see glucoses).

Acetyl Carbinol, *pyroracemic alcohol*, *acetone alcohol*, *oxyacetone*, *methylketol*, *acetol*, [*Propanolon*], $CH_3 . CO\ CH_2OH$, boiling at 145–150°, is a colorless oil with a feeble, peculiar odor. It is produced when water and freshly-precipitated barium carbonate act upon chloracetone (B. **24**, R. 726); also upon fusing cane and grape sugar with caustic potash (B. **16**, 837). Acetol and its ethers, when in solution, reduce alkaline copper solutions (B. **13**, 2344).

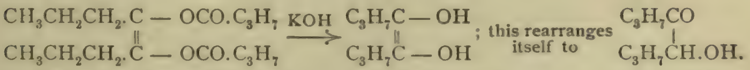
The *ethyl ether* boils at 128° (A. **269**, 14; B. **27**, R. 796). The *acetyl ester* boils at 172°. The *benzoyl ester* melts at 24°.

Phenyl Acetol, $C_6H_5O . CH_2 . CO . CH_3$, boils at 230° (B. **28**, 1253). *Ethyl Ketol*, $C_2H_5 . CO . CH_2OH$, boiling at 155–156°, is produced when *tetrinic acid* (see this) is heated with water to 200° (B. **26**, 2220; A. **288**, 19).

Chlor-, brom-, and iodo-acetone are the haloid esters of acetyl carbinol (p. 217). When the *a*- or 1 2-diketones, *diacetyl* and *acetyl propionyl* (p. 322), are reduced with zinc and sulphuric acid, the two ketone alcohols corresponding to benzoïn of the benzene series are produced (B. **22**, 2214; **23**, 2425).

Acetyl-methyl Carbinol, Dimethyl Ketol, [2.3-Butanolon], $CH_3COCH(OH)CH_3$, boils at 142°. *Acetyl-ethyl Carbinol*, $CH_3CO . CH(OH)CH_2 . CH_3$, boils at 77° (35 mm.). *Homologous acetols*, $R . CO . CH_2OH$, have been prepared in the form of their ethers from the halogen derivatives of alkylized acetoacetic esters (B. **21**, 2648).

Dibutyryl and *Di-isovaleryl* were described in connection with the saturated glycols. These are compounds which, upon saponification, do not yield unsaturated glycols, but their isomeric *a*- or 1.2-ketone alcohols:



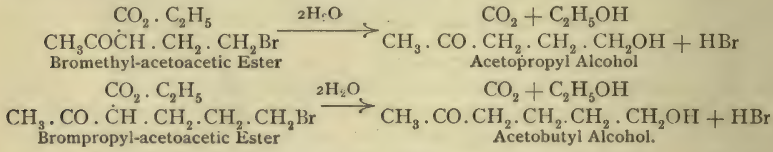
$$\begin{matrix}CH_3CH_2CH_2.C-OCO.C_3H_7\\ \| \\ CH_3CH_2CH_2.C-OCO.C_3H_7\end{matrix} \xrightarrow{KOH} \begin{matrix}C_3H_7C-OH\\ \| \\ C_3H_7C-OH\end{matrix}\ \text{; this rearranges itself to}\ \begin{matrix}C_3H_7CO\\ | \\ C_3H_7CH.OH.\end{matrix}$$

Butyroïn, $C_3H_7COCH(OH)C_3H_7$, boils at 180–190°, with slight decomposition.

Valeroïn, $C_4H_9CO . CH(OH)C_4H_9$, boils at 155–156° (12 mm.) (B. **24**, 1271).

When these ketols are treated with concentrated caustic potash and air, *Dipropyl*- and *Di-isobutylglycollic Acid*, $(C_4H_9)_2C(OH)CO_2H$ (compare benzoïn) result.

β- or 1.3-**Ketols.**—By the aldol condensation, acetaldehyde and chloral, together with acetone, yield the two ketols: *hydracetyl acetone*, $CH_3 . CH(OH) . CH_2 . CO . CH_3$, boiling at 176–177°, and *chloral acetone*, $CCl_3CH(OH) . CH_2 . CO . CH_3$, melting at 75–76° (B. **25**, 3165; **26**, 354, 908). *Diacetone Alcohol*, $(CH_3)_2C(OH)CH_2 . COCH_3$, also belongs in this group. It boils at 164°, and results from diacetonamine (p. 219) by the action of nitrous acid. The β- or 1.3-ketols lose water and pass into unsaturated ketones (p. 221), γ- or 1.4-*ketols* and δ- or 1.5-*Ketols.* Representatives of these ketol classes result from the products arising in the action of ethylene bromide and trimethylene bromide upon sodium acetoacetic ester; when bromethyl and brompropyl acetoacetic esters are boiled with hydrochloric acid (B. **19**, 2844; **21**, 2647; **22**, 1196, R. 572):



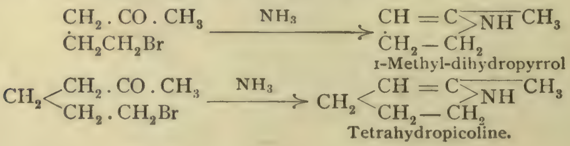
$$\underset{\text{Bromethyl-acetoacetic Ester}}{CH_3CO\overset{CO_2 . C_2H_5}{\dot{C}H} . CH_2 . CH_2Br} \xrightarrow{2H_2O} \underset{\text{Acetopropyl Alcohol}}{CH_3 . CO . CH_2 . CH_2 . CH_2OH} + HBr + CO_2 + C_2H_5OH$$

$$\underset{\text{Brompropyl-acetoacetic Ester}}{CH_3 . CO . \overset{CO_2 . C_2H_5}{\dot{C}H} . CH_2.CH_2.CH_2Br} \xrightarrow{2H_2O} \underset{\text{Acetobutyl Alcohol.}}{CH_3 . CO . CH_2 . CH_2 . CH_2 . CH_2OH} + HBr + CO_2 + C_2H_5OH$$

(1) *β-Acetopropyl Alcohol*, $CH_3 . CO . CH_2 . CH_2 . CH_2OH$, boils at 208° with decomposition.

(2) *γ-Acetobutyl Alcohol*, $CH_3 . CO . CH_2 . CH_2 . CH_2 . CH_2OH$, decomposes about 155°.

These compounds when heated give off water and become oxides of the unsaturated glycols (p. 298). Both ketone alcohols fail to reduce an ammoniacal copper solution, but when oxidized with chromic acid yield the corresponding carboxylic acids: *lævulinic acid* (see this) and *γ-acetobutyric acid* (see this). They yield the corresponding glycols, γ-pentylene glycol and δ-hexylene glycol, when reduced. Hydrobromic acid converts them into *brompropyl-methyl ketone*, $CH_3 . CO . CH_2 . CH_2 . CH_2Br$, and *brombutyl-methyl ketone*, $CH_3CO . CH_2 . CH_2 . CH_2 . CH_2Br$, boiling at 216°. These bromides are converted by ammonia into ring-shaped imides (B. **25**, 2190), similar to the γ-diketones (p. 324). This reaction links the open, aliphatic compounds with the pyrrol and pyridine derivatives:



$$\begin{matrix} CH_2 . CO . CH_3 \\ \dot{C}H_2CH_2Br \end{matrix} \xrightarrow{NH_3} \begin{matrix} CH = C \overline{\gt NH} CH_3 \\ \dot{C}H_2 - \dot{C}H_2 \end{matrix}$$

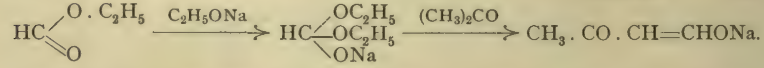
1-Methyl-dihydropyrrol

$$CH_2 < \begin{matrix} CH_2 . CO . CH_3 \\ CH_2 . CH_2Br \end{matrix} \xrightarrow{NH_3} CH_2 < \begin{matrix} CH = C \overline{\gt NH} CH_3 \\ CH_2 - CH_2 \end{matrix}$$

Tetrahydropicoline.

B. UNSATURATED KETOLS, OXYMETHYLENE KETONES.

Compounds of this class are obtained from the ketones $R . CO . CH_3$ and $R . CO . CH_2R'$, together with formic ester in the presence of sodium ethylate. It is very probable that at first the sodium compound of diethyl orthoformic acid is formed (p. 233), which is transposed by the ketone, and water is split off:



$$HC \begin{matrix} \diagup O . C_2H_5 \\ \diagdown O \end{matrix} \xrightarrow{C_2H_5ONa} HC \begin{matrix} \diagup OC_2H_5 \\ - OC_2H_5 \\ \diagdown ONa \end{matrix} \xrightarrow{(CH_3)_2CO} CH_3 . CO . CH{=}CHONa.$$

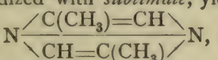
These bodies were at first thought to be β-ketoaldehydes. However, their pronounced acid character has shown that they should be regarded as oxymethylene ketones, acivinyl alcohols (Claisen, B. **20**, 2191; **21**, R. 915; **22**, 533, 3273; **25**, 1781). They dissolve in alkaline carbonates, forming stable salts, and give green colored precipitates with copper acetate (B. **22**, 1018). Acetic anhydride and benzoyl chloride converts them as readily in a free state as the phenols into neutral acetates and benzoates, insoluble in alkalies. Their alkali derivatives and ethyl iodide yield *oxyethyl ethers*, which are saponified by alcoholic alkalies, like the ethers of organic carboxylic acids. These compounds, $—CO.CH=CH.OH$, are the first exceptions to the rule of Erlenmeyer (p. 53), according to which the complex $>C=CHOH$ present in open chains must invariably rearrange itself into the *aldehyde form* $>CH.CHO$. It is shown, on the contrary, that when an hydrogen atom of the methyl or methylene group in acetaldehyde or its homologues, $R.CH_2.CHO$, is replaced by an acid radical, a rearrangement of the aldehyde form into the *vinyl alcohol form* is sure to follow (B. **25**, 1781).

In conjunction with this explanation it may be mentioned that the alkyl oxymethylene group—*e. g.*, $C_2H_5O.CH=$ —may be introduced by means of orthoformic ester and acetic anhydride into compounds which contain the atomic grouping, $—CO.CH_2.CO$ (B. **26**, 2729), *e. g.*, into acetyl acetone, acetoacetic ester and malonic ester. The compounds which result will be described subsequently in their proper places.

Oxymethylene Acetone (formerly called *formyl acetone*, *acetoacetic aldehyde*), $CH_3-CO.CH=CHOH$, boils at about 100°, and readily condenses in solution to [1.3.5]-*triacetyl benzene*, $C_6H_3[1.3.5-](CO.CH_3)_3$ (see this). Hydrazine converts it into 3-methyl pyrazole, and phenylhydrazine into 1-phenyl-3-methyl pyrazole (see this). *Oxymethylene-diethyl ketone*, $C_2H_5CO.C(CH_3)=CHOH$, melts at 40° and boils at 164–166°.

NITROGEN-CONTAINING DERIVATIVES OF THE KETONE ALCOHOLS.

(1 A) **Amidoketones** of the paraffin series are obtained by the reduction of isonitroso-ketones with stannous chloride (B. **27**, 1037). *Amidoacetone*, $CH_3.CO.CH_2-NH_2$, is a brown, thick oil. *Amidopropylmethyl ketone*, $CH_3COCH(NH_2)C_2H_5$, is an oil which solidifies to a crystalline mass.

Diacetonamine, $(CH_3)_2C(NH_2)CH_2.CO.CH_3$. Compare p. 219. These compounds, oxidized with *sublimate*, yield pyrazine derivatives; thus, **amido-acetone** passes into  $N\genfrac{}{}{0.4pt}{}{\diagup C(CH_3)=CH \diagdown}{\diagdown CH=C(CH_3) \diagup}N$, *dimethylpyrazine* (B. **27**, R. 928). The *pyrazines*, *ketines* or *aldines* will be treated along with the heterocyclic compounds. The hydrochlorides of the α-amidoketones are easily transposed by potassium cyanate into *imidazolones*, and by potassium sulphocyanide into *imidazolylmercaptans* (B. **27**, 1042, 2036).

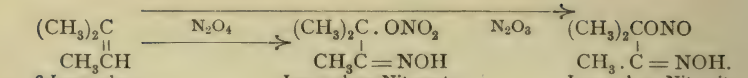
Dialkylamidoketones have been prepared in great number by the interaction of chloracetone and secondary amines: *Dimethylamido-acetone*, $(CH_3)_2N.CH_2.CO.-CH_3$, boils at 123°, while *Diethylamidoacetone* boils at 155° (B. **29**, 866).

(1 B) **Unsaturated β-Amidoketones** have been obtained from acetyl acetone (p. 323) by the action of ammonia, primary and secondary alkylamines (B. **26**, R. 290). *Acetylacetonamine*, $CH_3.CO.CH=C(NH_2)CH_3$, melts at 43° and boils at 209°. **Acetyl-acetone-ethylamine** $CH_3.CO.CH=C(NHC_2H_5)CH_3$, boils at 210–215°. **Acetyl-acetone diethylamine**, $CH_3.CO.CH=CN(C_2H_5)_2.CH_3$, boils at 155° (24 mm.).

(2) **Isoxazoles**, the anhydrides of the oximes of unsaturated β-oxyketones and β-oxyaldehydes will be subsequently treated together with the oximes of the aldehyde ketones and the diketones (p. 325).

(3) **α-Halogenketoximes** are produced by the action of hydroxylamine upon monohalogen acetones (p. 216). *Chloracetoxime*, $CH_2Cl.C:N(OH).CH_3$, boils at 71° (9 mm.); *bromacetoxime* melts at 36°, while *iodoacetoxime* melts at 64° (B. **29**, 1550).

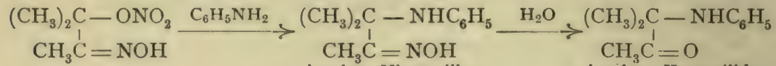
(4) **Alkylen Nitrosates and Nitrosites**, produced by the action of nitrogen tetroxide and trioxide upon alkylens, are nitrogen-containing derivatives of the α-ketols (A. **241**, 288; **245**, 241; **248**, 161; B. **20**, R. 638; **21**, R. 622), *e. g.*:



$$\begin{array}{ccccc} (CH_3)_2C & \xrightarrow{N_2O_4} & (CH_3)_2C.ONO_2 & \xrightarrow{N_2O_3} & (CH_3)_2CONO \\ \| & & | & & | \\ CH_3CH & & CH_3C{=}NOH & & CH_3.C{=}NOH. \end{array}$$

β-Isoamylene Trimethyl Ethylene — Isoamylene Nitrosate, m. p. 97° — Isoamylene Nitrosite.

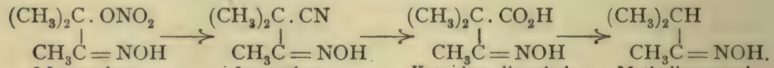
When amines act upon these bodies the O . NO_2 group is replaced by the NHR group with the formation of *nitrolamines*, from which *ketoamines* can be obtained:



$$\begin{array}{ccccc} (CH_3)_2C{-}ONO_2 & \xrightarrow{C_6H_5NH_2} & (CH_3)_2C{-}NHC_6H_5 & \xrightarrow{H_2O} & (CH_3)_2C{-}NHC_6H_5 \\ | & & | & & | \\ CH_3C{=}NOH & & CH_3C{=}NOH & & CH_3C{=}O \end{array}$$

Amylene Nitroaniline m. p. 131° — Amylene Ketoanilide.

Potassium cyanide introduces the cyanogen group for the—ONO_2 group of the amylene nitrosate, and from the nitrile an oxime acid may be prepared. The latter melts at 97° and breaks down into CO_2, and methyl isopropyl ketoxime, which would clear up the constitution of these bodies:



$$\begin{array}{ccccccc} (CH_3)_2C.ONO_2 & & (CH_3)_2C.CN & & (CH_3)_2C.CO_2H & & (CH_3)_2CH \\ | & \longrightarrow & | & \longrightarrow & | & \longrightarrow & | \\ CH_3C{=}NOH & & CH_3C{=}NOH & & CH_3C{=}NOH & & CH_3C{=}NOH. \end{array}$$

β-Isoamylene Nitrosate — Isoamylene Isonitrosocyanide — Ketoxime-dimethyl Acetoacetic Acid — Methylisopropyl Ketoxime.

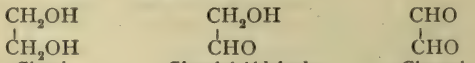
The nitrosate and nitrosite reactions are important for some of the terpenes (see these).

(5) **Pyrazoles** (see these) are heterocyclic nitrogen-containing derivatives of the unsaturated β-oxyketones (p. 318), which are obtained from these and hydrazine or phenylhydrazine (see above).

4. DIALDEHYDES.

The only known dialdehyde of the fatty series is glyoxal, discovered in 1856 by Debus.

Glyoxal, Oxalaldehyde [Ethandial], Diformyl, CHO . CHO, is the dialdehyde of ethylene glycol and oxalic acid, while glycolyl aldehyde (p. 315) represents the first or half aldehyde of ethylene glycol and the aldehyde of glycollic acid:



$$\begin{array}{ccc} CH_2OH & CH_2OH & CHO \\ | & | & | \\ CH_2OH & CHO & CHO \end{array}$$

Glycol — Glycolyl Aldehyde — Glyoxal.

Glyoxal, glycollic acid and glyoxylic acid are formed in the careful oxidation of ethylene glycol, ethyl alcohol (B. **14**, 2685; **17**, R. 168), or acetaldehyde with nitric acid. It may also be prepared by transposing its sodium salt with sodium bisulphite (B. **24**, 3235).

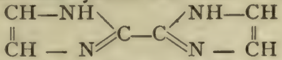
On evaporating the solutions the glyoxal is obtained as an amorphous, non-volatile mass. It deliquesces in the air. It is very soluble in both alcohol and ether. In this condition it probably represents a hydrate, because *methylglyoxal* (p. 321) and *dimethyl glyoxal* (p. 322) are very volatile (B. **21**, 809).

Deportment: The alkalies convert it, even in the cold, into glycollic acid. In this change the one CHO group is reduced, while the other is oxidized (compare benzil and benzilic acid):

$$\begin{array}{l}CHO\\ |\\ CHO\end{array} + H_2O = \begin{array}{l}CH_2OH\\ |\\ CH_2OH.\end{array}$$

As a dialdehyde it unites directly with 2 molecules of primary sodium sulphite, forming the crystalline compound, $C_2H_2O_2(SO_3HNa)_2 + H_2O$. This bisulphite is readily transposed by primary and secondary amines, with the production either of derivatives of glycocoll or indolsulphonic acids (B. **27**, 3258). It also reduces ammoniacal silver solutions.

Concentrated ammonia yields two bases with glyoxal: **Glycosin,**



(B. **20**, R. 431),

and in larger quantity, **Glyoxaline,** $C_3H_4N_2$, the parent substance of the glyoxalines (oxalines) or amidazoles (β-diazoles) (see these).

For their deportment with *o*-phenylenediamine compare the α-diketones, page 322. **Glyoxime,** page 327. **Glyoxalosazone,** p. 328. Glyoxal and urea form a diureïde called *glycoluril*.

Nucleus-synthetic Reactions.—Formic aldehyde and acetaldehyde unite with hydrocyanic acid to form the nitriles of glycollic and lactic acids respectively. Glyoxal in the same manner combines with prussic acid and becomes the nitrile of racemic acid. Consult B. **21**, R. 636, for the condensation of glyoxal with malonic ester and acetoacetic ester.

Orthoglyoxal diethylene ether, $\begin{array}{l}CH_2\,.\,O\,.\,CH\,.\,O\,.\,CH_2\\ |\qquad\quad\;\; |\qquad\quad\; |\\ CH_2\,.\,O\,.\,CH\,.\,O\,.\,CH_2\end{array}$, melting at 134°, is produced by the action of hydrochloric acid gas upon glycol and glyoxal (B. **28**, R. 321).

Other aldehydes of saturated dibasic acids are not known. γ-Butyrolactone was formerly thought to be the dialdehyde of succinic acid.

Dibrom-maleïc aldehyde, $OCH\,.\,CBr:CBr\,.\,CHO$, melting at 69°, has been formed by the action of bromine water upon $\beta\gamma$-dibrompyroracemic acid (A. **232**, 89).

The oximes, hydrazones, and osazones will all be treated together with the corresponding derivatives of the aldehyde ketones and diketones (p. 325).

5. KETONE ALDEHYDES or ALDEHYDE KETONES.

Pyroracemic Aldehyde, *Acetyl Formyl, Methyl Glyoxal* [Propanalon], $CH_3\,.\,CO\,.\,CHO$, is a yellow volatile oil, obtained by boiling its monoxime, isonitrosoacetone (p. 326), with dilute sulphuric acid. The bodies formerly supposed to be β-ketone aldehydes, which were also called formyl ketones, *e.g.*, formyl acetone $CH_3\,.\,CO\,.\,CH_2\,.\,CHO$, have been found to be unsaturated ketols; they have, therefore, been already discussed in connection with the saturated ketols.

6. DIKETONES.

The relative position of the CO-groups determines them to be either α- or 1.2-diketones, β- or 1.3-diketones, γ- or 1.4-diketones, etc.

They have been regarded as diketosubstitution products of the paraffins, hence the name. The "Geneva names" contain the syllable "di" between the paraffin name and the ending "on"; thus [Butandion] for $CH_3\,.\,CO\,.\,COCH_3$. The α-diketones are most generally designated as compounds of two acid radicals, *e. g.*, *diacetyl* for $CH_3CO\,.\,CO\,.\,CH_3$; the β-diketones as monoketones containing acid radicals, *e. g.*, acetyl acetone, $CH_3\,.\,CO\,.\,CH_2\,.\,CO\,.\,CH_3$.

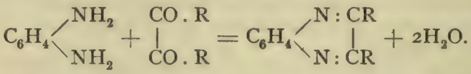
The diketones react like the monoketones with hydroxylamine and phenylhydrazine. Their oximes, prepared in another manner, constitute the chief starting-out material for the obtainment of the *a*-diketones. The nitrogen-containing derivatives of the diketones, the aldehyde ketones and dialdehydes, because of their importance, will be discussed after the diketones.

(1) *a*-**Diketones or 1.2-Diketones.**

These are obtained from their monoximes, the isonitrosoketones, by boiling the latter with dilute sulphuric acid (v. Pechmann) (B. **20**, 3213; **21**, 1411; **22**, 527, 532; **24**, 3954); see *pyroracemic aldehyde*. They are also formed when the monoketones are oxidized with nitric acid (B. **28**, 555).

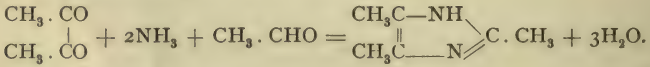
The *a*-diketones, in contradistinction to the colorless aliphatic monoketones are yellow, volatile liquids with a penetrating quinone-like odor.

(1) The *a*-diketones are characterized and distinguished from the β- and γ-ketones by their ability to unite with the orthophenylenediamines (similar to glyoxal). In this way they are condensed to the *quinoxalines* (see these):



$$C_6H_4\begin{cases}NH_2\\ NH_2\end{cases}+\begin{array}{l}CO.R\\ \,|\\ CO.R\end{array}=C_6H_4\begin{cases}N:CR\\ \quad\;\;|\\ N:CR\end{cases}+2H_2O.$$

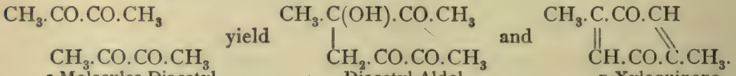
All compounds containing the group —CO . CO—, *e. g.*, glyoxal, pyroracemic acid, glyoxylic acid, alloxan, dioxytartaric acid, etc., react similarly with the *o*-phenylenediamines. (2) The *glyoxalines* are the products of the union of the *a*-diketones with ammonia and the aldehydes:



$$\begin{array}{l}CH_3.CO\\ \quad\;\;|\\ CH_3.CO\end{array}+2NH_3+CH_3.CHO=\begin{array}{l}CH_3C-NH\\ \quad\;\;\|\\ CH_3C-\!\!-N\end{array}\!\!\!>C.CH_3+3H_2O.$$

(3) *Nucleus-synthetic reactions:*

a-Diketones, containing a CH_2-group, together with the CO-group, sustain a rather remarkable condensation when acted upon by the alkalies. *Aldols* are first produced, and later the *quinones* (B. **22**, 2215; **28**, 1845):



$$\begin{array}{l}CH_3.CO.CO.CH_3\\ \\ \quad CH_3.CO.CO.CH_3\end{array}\text{ yield }\begin{array}{l}CH_3.C(OH).CO.CH_3\\ \quad|\\ CH_2.CO.CO.CH_3\end{array}\text{ and }\begin{array}{l}CH_3.C.CO.CH\\ \quad\;\;\|\qquad\;\;\backslash\backslash\\ \quad\;\;CH.CO.C.CH_3.\end{array}$$

2 Molecules Diacetyl Diacetyl Aldol p-Xyloquinone.

(4) Diacetyl and prussic acid yield the nitrile of dimethyl racemic acid (see glyoxal) (B. **22**, R. 137).

Diacetyl, $CH_3 . CO . CO . CH_3$, **Diketobutane, Dimethyl diketone**, dimethyl glyoxal [Butandion], from isonitrosoethylmethylketone, has also been obtained from oxalyldiacetic acid (ketipic acid) by the splitting-off of the carboxyls upon the application of heat (B. **20**, 3183), as well as by the oxidation of tetrinic acid (see this) with $KMnO_4$ (B. **26**, 2220; A. **288**, 27). It is a yellow liquid, with an odor like that of quinone. It boils at 87–89°.

Tetrachlor-diacetyl, $CHCl_2 . CO . CO . CHCl_2$, results in the action of potassium chlorate upon chloranilic acid (together with tetrachloracetone, p. 217). It melts at 84° (B. **22**, R. 809; **23**, R. 20).

Tetrabrom-diacetyl $(CHBr_2 . CO)_2$ (B. **23**, 35) and **Dibrom-diacetyl**, $(CH_2Br . CO)_2$, are produced by the action of bromine upon diacetyl.

Acetyl-propionyl, $C_2H_5 . CO . CO . CH_3$, **Methyl-ethyl-diketone**, [2.3-pentandion], from isonitroso-ethylacetone, condenses to duroquinone. It boils at 108°.

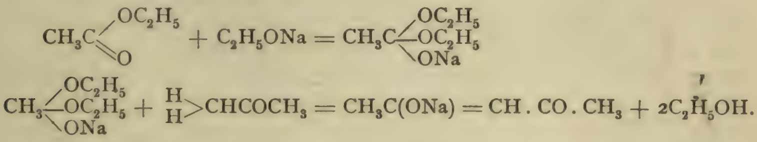
Acetyl-butyryl, [2 3-Hexandion], $C_3H_7 . CO . CO . CH_3$, boils at 128°. **Acetyl-iso-butyryl**, $(CH_3)_2CHCO . CO . CH_3$, boils at 115°. *Acetyl isovaleryl*, $(CH_3)_2CHCH_2COCOCH_3$, boils at 138°. *Acetyl Iso-caproyl*, $(CH_3)_2CHCH_2CH_2COCOCH_3$, boils at 163° (B. **22**, 2117; **24**, 3956).

a-Diketone Dichlorides result in the action of hypochlorous acid upon alkylized acetylenes (p. 97), according to the equation :

$$C_2H_5 . C \vdots C . CH_3 + 2ClOH = C_2H_5 . CCl_2 . CO . CH_3 + H_2O.$$

Methyl-a-dichlorpropyl Ketone, $C_2H_5 . CCl_2 . CO . CH_3$, boiling at 138°, yields methyl-n-propyl ketone on reduction ; with a potash solution it forms duroquinone, angelic acid (p. 283), and α-ethyl acrylic acid. The two acids result from an intramolecular atomic rearrangement which recalls that of the formation of benzilic acid from benzil (p. 54).

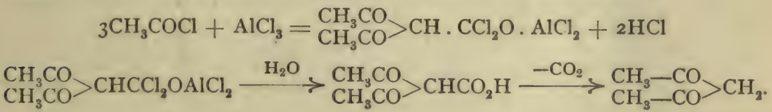
(2) β- or 1.3-**Diketones** are produced according to two nucleus-synthetic reactions : (1) Like the oxymethylene ketones, by the interaction of acetic esters and ketones in the presence of sodium ethylate, or, better, metallic sodium (Claisen, B. **22**, 1009 ; **23**, R. 40). It is very probable that the formation of a sodium derivative of orthoacetic acid precedes the condensation. Compare oxymethylene ketones (p. 318) and acetoacetic ester (see this) :



$$CH_3C\begin{matrix}\diagup OC_2H_5\\ \diagdown O\end{matrix} + C_2H_5ONa = CH_3C\begin{matrix}\diagup OC_2H_5\\ -OC_2H_5\\ \diagdown ONa\end{matrix}$$

$$CH_3\begin{matrix}\diagup OC_2H_5\\ -OC_2H_5\\ \diagdown ONa\end{matrix} + \begin{matrix}H\\ H\end{matrix}{>}CHCOCH_3 = CH_3C(ONa) = CH . CO . CH_3 + 2C_2H_5OH.$$

(2) By the action of $AlCl_3$ upon acetyl chloride and the subsequent decomposition of the aluminium derivative. This reaction was discovered by Combes, but correctly interpreted by Gustavson (B. **21**, R. 252 ; **22**, 1009) :



$$3CH_3COCl + AlCl_3 = \begin{matrix}CH_3CO\\ CH_3CO\end{matrix}{>}CH . CCl_2O . AlCl_2 + 2HCl$$

$$\begin{matrix}CH_3CO\\ CH_3CO\end{matrix}{>}CHCCl_2OAlCl_2 \xrightarrow{H_2O} \begin{matrix}CH_3CO\\ CH_3CO\end{matrix}{>}CHCO_2H \xrightarrow{-CO_2} \begin{matrix}CH_3{-}CO\\ CH_3{-}CO\end{matrix}{>}CH_2.$$

Constitution.—The β-diketones, like the oxymethylene ketones, (p. 318), have an acid character. Although the formyl ketones are regarded as oxymethylene derivatives, the disposition generally is to assign the salts of the β-diketones, *e. g.*, $CH_3 . CO . CH = C(ONa)CH_3$, the vinyl alcohol formula, retaining for the free ketones, however, the diketo-formula. Compare also acetoacetic ester (see this), and formylacetic ester (see this) (A. **277**, 162). The molecular refraction is an argument in favor of this view (B. **25**, 3074).

Deportment.—Their alkali salts are precipitated by copper acetate. Ferric chloride imparts an intense red color to their alcoholic solution. See pp. 327, 328 for their remarkable behavior with hydroxylamine and phenylhydrazine.

Acetyl-acetone, $CH_3 . CO . CH_2 . CO . CH_3$, boils at 137°. See above for its formation. It can be produced by electrolyzing an alcoholic solution of sodium acetyl acetone. Tetraacetylethane is formed by the action of iodine upon the same salt (B. **26**, R. 884). S_2Cl_2 and SCl_2 produce dithio- and monothio-acetyl acetone (B. **27**, R. 401, 789). See p. 328 for the action of hydrazine and phenylhydrazine. *Copper Acetyl Acetone*, $(C_5H_7O_2)_2Cu$. *Beryllium Acetyl Acetone* $(C_5H_7O_2)_2Be$, melts at 108° and boils at 270°. *Aluminium Acetyl Acetone*, $(C_5H_7O_2)_3Al$, melts at 193° and boils at 314°. The vapor densities of these bodies indicate the bivalent nature of glucinum, and the trivalent character of aluminium (Combes, B. **28**, R. 10). *Octochloracetyl Acetone* melts at 43°. *Octobromacetyl Acetone*, $CBr_3 . COCBr_2COCBr_3$, is formed when chlorine or bromine acts upon phloroglucin. It melts at 154° (B. **23**, 1717).

Alkylized acetyl acetones are produced when sodium and alkyl iodides act upon acetyl acetone (Combes, B. **20**, R. 285 ; **21**, R. 11).

Acetyl-methylethyl Ketone, $CH_3 . CO . CH_2 . CO . C_2H_5$, acetylpropionyl methane, boils at 158°.

Acetyl-methylpropyl Ketone, acetyl-butyryl methane, boils at 175° (B. **22,** 1015).

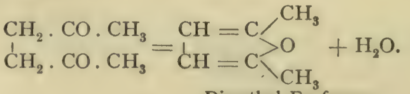
(3) γ- or 1.4-Diketones.

These correspond to the paraquinones of the aromatic series (see these). They are not capable of forming salts, hence are not soluble in the alkalies. They form mono- and di-oximes with hydroxylamine, and mono- and di-hydrazones with phenylhydrazine; these are colorless. The readiness with which the γ-diketones form pyrrol, furfurane, and thiophene derivatives is characteristic of them.

Acetonyl Acetone, s Diacetylethane, [2.5-Hexandion], $CH_3 . CO . CH_2 . CH_2 . CO . CH_3$, is obtained from pyrotritartaric acid, $C_7H_8O_3$ (see this), and from *acetonyl acetoacetic ester* (see this), upon heating to 160° with water (B. **18,** 58), and from isopyrotritartaric acid and diacetylsuccinic ester, when they are allowed to stand in contact with sodium hydroxide (B. **22,** 2100). A liquid with an agreeable odor. It is miscible with water, alcohol, and ether. It boils at 194° C.

Conversion of Acetonyl Acetone into 1.4-Dimethyl-furfurane, -thiophene, and -pyrrol (Paal, B. **18,** 58, 367, 2251).

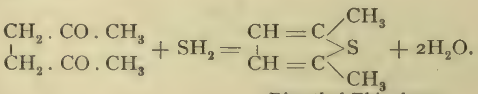
(1) The direct removal of one molecule of water from acetonyl acetone (by distillation with zinc chloride or P_2O_5) affords dimethyl furfurane (B. **20,** 1085):



Dimethyl Furfurane.

Other γ-diketone compounds react in a similar manner (Knorr, B. **17,** 2756).

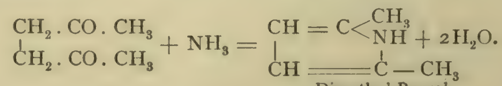
(2) When heated with phosphorus sulphide acetonyl acetone yields dimethyl thiophene:



Dimethyl Thiophene.

All the γ diketones or (1.4)-dicarboxyl compounds, *e. g.*, the γ-ketonic acids (see these), yield the corresponding thiophene derivatives upon like treatment (B. **19,** 551).

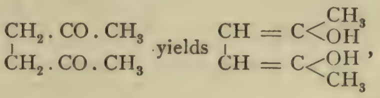
(3) *Dimethyl pyrrol* is produced on heating acetonyl acetone with alcoholic ammonia:



Dimethyl Pyrrol.

All compounds containing two CO-groups in the (1.4) position react similarly with ammonia and amines. Such are diaceto-succinic ester and lævulinic ester. All the pyrrol derivatives formed as above, when boiled with dilute mineral acids, have the power of coloring a pine chip an intense red. This reaction is, therefore, a means of recognizing all (1.4)-diketone compounds (B. **19**, 46). These derivatives react similarly with amidophenols and amido-acids (B. **19**, 558).

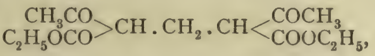
In all these conversions of acetonyl acetone into pyrrol, thiophene, and furfurane derivatives it may be assumed that it first passes from the diketone form into the pseudo-form of the unsaturated diglycol (p. 57):



$$\begin{matrix} CH_2 . CO . CH_3 \\ | \\ CH_2 . CO . CH_3 \end{matrix} \text{ yields } \begin{matrix} CH = C<^{CH_3}_{OH} \\ | \\ CH = C<^{OH}_{CH_3} \end{matrix},$$

and from this, by replacing the 2OH groups with S, O, or NH, the corresponding furfurane, thiophene, and pyrrol compounds are produced (B. **19**, 551).

1.5- or δ-**Diketones** are not known. If it is attempted to prepare them from the δ-diketone dicarboxylic esters, *e. g.*, *aa*-diacetyl glutaric ester:



$$\begin{matrix} CH_3CO \\ C_2H_5OCO \end{matrix}\!>CH . CH_2 . CH<\!\begin{matrix} COCH_3 \\ COOC_2H_5 \end{matrix},$$

resulting from the condensation of aldehydes and acetoacetic esters, by splitting off carboxyethyl groups, there results instead of, for example, diacetylpropane or 2.5-heptandion, $CH_3 . CO . CH_2 . CH_2 . CH_2 . CO . CH_3$, a carbocyclic condensation product—3-Methyl-Δ_2-R-hexene (A. **288**, 321).

ζ-**Diketone** (1.7). Diacetyl Pentane, $CH_3 . CO(CH_2)_5CO . CH_3$, belongs to this class. When this is reduced, it sustains an intramolecular pinacone formation and becomes **dimethyldihydroxyheptamethylene**, $CH_3 . \overline{\overset{|}{C}(OH)(CH_2)_5\overset{|}{C}}(OH)CH_3$ (B. **23**, R. 249; **24**, R. 634; **26**, R. 316).

NITROGEN-CONTAINING DERIVATIVES OF THE DIALDEHYDES, ALDEHYDE KETONES, AND DIKETONES.

1. For the action of ammonia upon glyoxal and acetonyl acetone, consult pp. 321, 324.

2. **Oximes.**

A. **Monoximes.**—(*a*) *Aldoximes of the a-aldehyde ketones and monoximes of the a-diketones: isonitrosoketones or oximido-ketones.* These bodies are formed (1*a*) by the action of nitrogen trioxide upon ketones (B. **20**, 639).

(1*b*) When amyl nitrite in the presence of sodium ethylate or hydrochloric acid acts upon ketones. At times sodium ethylate and again hydrochloric acid gives the best yield (B. **20**, 2194; **28**, 1915):

$$CH_3 . CO . CH_3 + NO . O . C_5H_{11} = CH_3 . CO . CH(N . OH) + C_5H_{11} . OH.$$

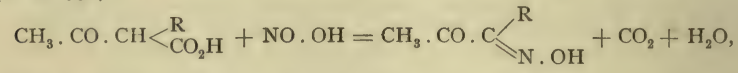
An excess of amyl nitrite decomposes the oximido-body, in that the oximido-group is replaced by oxygen, with the production of a-diketo-derivatives (B. **22**, 527).

(2) Just as acetone is formed from acetoacetic ester, so can isonitroso- or oximido-

acetone be prepared from the oximido-derivative of acetoacetic ester (B. **15**, 1326). Nitrous acid decomposes acetoacetic acid into oximido-acetone and carbon dioxide:

$$CH_3 . CO . CH_2 . CO_2H + NO . OH = CH_3 . COCH(N . OH) + CO_2 + H_2O.$$

Similarly, the oximido-compounds of the higher acetones can be directly derived from the monoalkylic acetoacetic acids and their esters by the exit of carbon dioxide (B. **20**, 531):



$$CH_3 . CO . CH{<}{\genfrac{}{}{0pt}{}{R}{CO_2H}} + NO . OH = CH_3 . CO . C{\genfrac{}{}{0pt}{}{\diagup R}{\diagdown N . OH}} + CO_2 + H_2O,$$

while the dialkylic acetoacetic acids do not react (B. **15**, 3067).

Properties.—The isonitroso- or oximido-ketones are colorless, crystalline bodies, easily soluble in alcohol, ether and chloroform, but usually more sparingly soluble in water. They dissolve in the alkalies, the hydrogen of the hydroxyl group being replaced by metal, with the formation of salts having an intensely yellow color. They yield a yellow coloration with phenol and sulphuric acid, and not the blue coloration of the nitroso-reaction (B. **15**, 1529).

Deportment.—(1) As in the keton-oximes, so also in the isonitroso-ketones, the oximido-group can be split off and be replaced by oxygen, which will lead to the formation of diketo bodies, —CO . CO—. Sodium bisulphite, and boiling the resulting imidsulphonic acid with dilute acids will bring about this transposition (B. **20**, 3162). The reaction also takes place when isonitroso-ketones are boiled directly with dilute sulphuric acid (B. **20**, 3213). The decomposition is sometimes more readily effected by nitrous acid (B. **22**, 532).

(2) The aldoximido-ketones, like the aldoximes (p. 206), are converted by dehydrating agents—*e. g.*, acetic anhydride—into acidyl cyanides or α-keton-carboxylic nitriles (see these) (B. **20**, 2196).

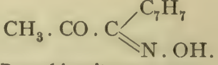
(3) *Amido-ketones* (p. 319) are produced in the reduction of isonitroso-ketones by means of stannous chloride.

(4) Two molecules of phenylhydrazine acting upon the isonitroso-ketones produce *osazones*, *e. g.*, $CH_3 . C(N_2H . C_6H_5)CH(N_2H . C_6H_5)$—acetonosazone (B. **22**, 528).

(5) By the further action of hydroxylamine or its hydrochloride (B. **16**, 182) upon isonitroso-acetone, the ketone oxygen is replaced and *ketoximic acids* or *dioximes* of the α-aldehyde ketones and α-diketones are produced.

(6) The *benzyl ether* results from the action of sodium alcoholate and benzyl chloride upon nitroso-acetone. This is isomeric with the benzyl-isonitroso-acetone derived from benzyl-aceto-acetic acid:

$CH_3 . CO . CH : N . OC_7H_7$ and



$$CH_3 . CO . C{\genfrac{}{}{0pt}{}{\diagup C_7H_7}{\diagdown N . OH.}}$$

Isonitroso-acetone-benzyl Ether **Benzyl-isonitroso-acetone.**

This is evidence that the oximide group, N . OH, is present in the isonitroso-compounds (B. **15**, 3073). Consult B. **16**, 835, for the salts of the isonitroso-ketones.

Isonitroso-acetone, aldoxime of pyroracemic aldehyde, $CH_3 . CO . CH : (N . OH)$, is very readily soluble in water; crystallizes in silvery, glistening tablets or prisms; fuses at 65°, and decomposes at higher temperatures, but may be volatilized in a current of steam. The aldehyde of pyroracemic acid, $CH_3 . CO . CHO$ (p. 296), can be obtained from it by splitting off the isonitroso-group.

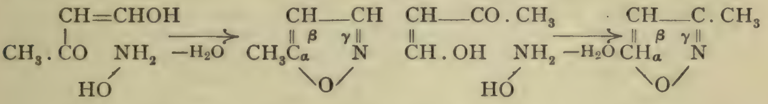
Monoximes of the α-Diketones.—*Isonitrosomethyl-acetone*, $CH_3 . CO . C = NOH . CH_3$, melts at 74° and boils at 185–188°. *Isonitrosomethylpropyl-ketone*, $CH_3CO . C = NOH . CH_2 . CH_3$, melts at 52–53° and boils at 183–187°. *Isonitroso-*

diethyl-ketone, $C_2H_5 . CO . C = N . OH . CH_3$, melts at 59–62°. *Isonitrosomethyl-butyl-ketone*, $CH_3 . CO . C = NOH . C_3H_7$, melts at 49.5°. *Isonitrosomethyl-isobutyl-ketone*, $CH_3 . CO . C = NOH . CH(CH_3)_2$, melts at 75°. *Isonitrosomethyl-isoamyl-ketone*, $CH_3 . CO . C = NOH . CH_2 . CH(CH_3)_2$, melts at 42° C. *Isonitrosomethyl-isocapryl-ketone*, $CH_3 . CO . C = NOH . CH_2 . CH_2 . CH(CH_3)_2$, melts at 38°.

B. Oxime-anhydrides of the β-Diketones or Isoxazoles.

Monoximes of the β-formylketones and of the β-diketones are not known. In the attempt to prepare them water splits off and an intramolecular anhydride formation takes place. The oxime-anhydrides are isomeric with the oxazoles, which also consist of five members; hence their name, *isoxazoles* (B. **21**, 2178; **24**, 390; **25**, 1787).

a-Methylisoxazole, CH_3-*a*-C_3H_2NO, boiling at 122°, and *γ-methylisoxazole*, CH_3-γ-C_3H_2NO, boiling at 118°, result from oxymethylene or formyl acetone. They are transparent liquids, having an intense odor, resembling that of pyridine. *a*-Methylisoxazole readily rearranges itself into cyanacetone (see this):

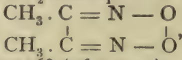


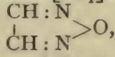
aγ-**Dimethylisoxazole** $(CH_3)_2$-*aγ*-C_3HNO, boiling at 141–142°, has a very peculiar odor, and is obtained from acetylacetone and hydroxylamine hydrochloride.

C. Dioximes.

(*a*) **Glyoximes** or *a*-**Dioximes.**—The monoxime of glyoxal is not known, but when it (pyroracemic aldehyde) and the *a*-diketones are treated with hydroxylamine hydrochloride, then the *a*-dioximes or glyoximes are formed. They can also be obtained from *a*-isonitroso-ketones or *a*-dichlorketones.

Glyoxime, $CH(=N . OH) . CH(=N . OH)$, melting at 178° (B. **17**, 2001; **25**, 705; **28**, R. 620), is prepared from trichlorlactic acid (p. 340). **Methyl Glyoxime, Acetoximic Acid,** $CH_3C(NOH) . CH(NOH)$, melts at 153°. **Dimethyl Glyoxime,** *Diacetyldioxime*, $CH_3C(NOH) . C(NOH)CH_3$, melts at 234° (B. **28**, R. 1006). *Methyl-ethyl Glyoxime*, $CH_3C(NOH) . C(NOH) . C_2H_5$, melts with decomposition at 170°. *Methyl-propyl Glyoxime* melts at 168°. *Methyl-isobutyl Glyoxime* melts at 170–172°.

(*b*) **Glyoxime Peroxides** (B. **23**, 3496) result when NO_2 acts upon an ethereal solution of the glyoximes: *dimethyl glyoxime peroxide*,  $\begin{matrix} CH_3 . C = N - O \\ | \qquad\quad | \\ CH_3 . C = N - O \end{matrix}$, boils at 222–223°. *Methyl-ethyl Glyoxime Peroxide* boils at 115–116° (16.5 mm.).

(*c*) **Furazanes,** *Azoxazoles*, *Furo*-[a.a$_1$]-*diazoles* are the anhydrides obtained from certain *a*-dioximes. Furazane,  $\begin{matrix} CH : N \\ | \\ CH : N \end{matrix} > O$, itself is not known, while *dimethyl-furazane*, for example, from diacetyl dioxime, has been prepared.

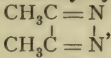
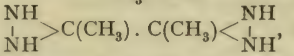
(*d*) β-**Dioximes** are not known (see above); they would be oxime anhydrides of the β-diketones or isoxazoles.

(*e*) γ-**Dioximes,** which may be systematically derived from the γ-dialdehydes (γ-butyrolactone, see this) and γ-aldehyde-ketones, not known in a free condition and probably not capable of existing, as well as from known γ-diketones, may be prepared (1) by the action of hydroxylamine upon pyrrol (B. **22**, 1968) and alkyl pyrrols (B. **23**, 1788); (2) from γ-diketones and hydroxylamine. They are decomposed by boiling alkalies into the corresponding acids, or γ-diketones.

Succinaldehyde-dioxime, $HO . N : CH . CH_2 . CH_2 . CH : N . OH$, melting at 173°, passes upon reduction into tetramethylene diamine (p. 313). *Ethylsuccinal-dioxime*, $HO . N : CH . CH(C_2H_5) . CH_2 . CH : N(OH)$, melts at 134–135°. *Propionyl-propional-dioxime*, $CH_3 . CH_2C : N(OH) . CH_2 . CH_2 . CH : N(OH)$, melts at 84–85°. *Methyl-lævulinal-dioxime*, $CH_3 . C : N(OH) . CH_2CH(CH_3)CH : N(OH)$. *Acetonyl-*

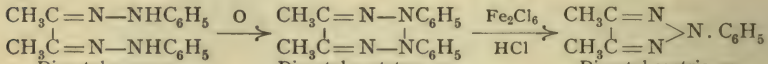
acetone-dioxime, $CH_3.C:N(OH)CH_2.CH_2C:N(OH).CH_3$, melts at 134–135°. *ωω-Diacetylpentan-dioxime*, $CH_3C:N(OH)(CH_2)_5C:N(OH)CH_3$, melts at 172°.

3. Hydrazine and Phenylhydrazine Derivatives.

Dimethylaziethane,  $\begin{array}{l}CH_3C=N\\ \ \ \ \ \ |\qquad |\\ CH_3C=N\end{array}$, melting above 270°, and *Dimethylbishydrazimethylene*,  $\begin{array}{l}NH\\ |\\ NH\end{array}\!>C(CH_3).C(CH_3)<\!\begin{array}{l}NH\\ |\\ NH\end{array}$, melting at 158°, are obtained from diacetyl and hydrazine (J. pr. Ch. [2] **44**, 174).

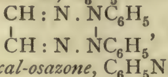
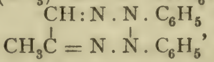
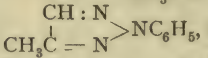
Monohydrazones.—Hydrazone of Pyroracemic Aldehyde, $CH_3CO.CH:N.NH.C_6H_5$, melting at 148°, is obtained by saponifying the reaction-product resulting from diazobenzene chloride and sodium acetoacetic ester with alcoholic caustic potash. **Diacetyl-hydrazone,** $CH_3.CO.C:N(NHC_6H_5)CH_3$, melting at 133°, has been prepared from diacetyl- and methyl-acetoacetic ester (Japp and Klingemann) (A. **247**, 190).

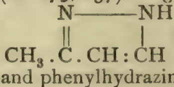
Dihydrazones or Osazones.—Glyoxal (p. 320), methyl-glyoxal (p. 322), the *a*-diketones and the *a*-isonitroso-acetones, when treated with phenylhydrazine, lose two molecules of water and form: diphenyl-hydrazones or **osazones**, which can also be obtained from *a*-oxyaldehydes, *a*-oxyketones, *a*-amidoaldehydes and *a*-amidoketones. The osazones have become especially important for the chemistry of the aldopentoses, and the aldo- and ketohexoses. The osazones are oxidized by potassium chromate and acetic acid to *osotetrazones*, which are converted by hydrochloric acid and ferric chloride into *osotriazones:*

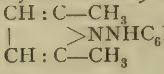


$$\begin{array}{l}CH_3C=N—NHC_6H_5\\ \ \ \ \ \ |\\ CH_3C=N—NHC_6H_5\end{array}\xrightarrow{O}\begin{array}{l}CH_3C=N—NC_6H_5\\ \ \ \ \ \ |\qquad\qquad |\\ CH_3C=N—NC_6H_5\end{array}\xrightarrow[HCl]{Fe_2Cl_6}\begin{array}{l}CH_3C=N\\ \ \ \ \ \ |\\ CH_3C=N\end{array}\!\!>N.C_6H_5$$

Diacetyl-osazone Diacetyl-osotetrazone Diacetyl-osotriazone.

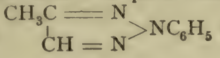
Glyoxal-osazone, $C_6H_5NHN:CH.CH:N.NHC_6H_5$, melts at 177°. *Glyoxal-osotetrazone*,  $\begin{array}{l}CH:N.NC_6H_5\\ |\qquad\quad |\\ CH:N.NC_6H_5\end{array}$, melts at 145° (B. **17**, 2001; **21**, 2752; **26**, 1045). *Methyl-glyoxal-osazone*, $C_6H_5NH.N:C(CH_3).CH:N.NHC_6H_5$, melts at 145° (B. **26**, 2203). *Methyl-glyoxal-osotetrazone*,  $\begin{array}{l}CH:N.N.C_6H_5\\ \ \ \ \ \ |\qquad\quad |\\ CH_3C=N.N.C_6H_5\end{array}$, melts at 106°–107°. *Methyl-glyoxal-osotriazone*,  $\begin{array}{l}CH:N\\ \ \ \ \ \ |\\ CH_3C=N\end{array}\!\!>NC_6H_5$, boils at 149–150° (60 mm.) (B. **21**, 2755). *Diacetyl-osazone* (formula above) melts with decomposition at 236° (B. **20**, 3184; A. **249**, 203). *Diacetyl-osotetrazone* (formula above) melts with decomposition at 169°. *Diacetyl-osotriazone* (formula above) melts at 35° and boils at 255° (B. **21**, 2759). *a-Acetyl-propionyl-hydrazone*, $CH_3C(:NNHC_6H_5)CO.C_2H_5$, from acetyl-propionyl, melts at 96–98°. *β-Acetyl-propionyl-hydrazone*, $CH_3.CO.C(:N-NHC_6H_5)C_2H_5$, from ethyl acetoacetic acid, melts at 116–117°. *Acetyl-propionyl-osazone* melts at 162° (B. **21**, 1414; A. **247**, 221).

The 1.3-diketones and the 1.3-oxymethylene ketones (p. 319) unite with hydrazine and phenylhydrazine, forming **pyrazoles** (see these), which may be regarded as derivatives of the 1.3-olefine ketols (A. **279**, 237): *e. g.*, oxymethylene acetone and hydrazine yield 3-**Methylpyrazole,**  $\begin{array}{l}\ \ \ \ \ \ \ N\text{———}NH\\ \ \ \ \ \ \ \ \|\qquad\quad\ |\\ CH_3.C.CH:CH\end{array}$ (B. **27**, 954).

Acetonyl-acetone, a 1.4-diketone, and phenylhydrazine yield: *Acetonyl acetonosazone*, melting at 120°, and *phenylamido-dimethyl-pyrrol*,  $\begin{array}{l}CH:C—CH_3\\ |\\ CH:C—CH_3\end{array}\!\!>NNHC_6H_5$, melting at 90° and boiling at 270° (B. **18**, 60; **22**, 170).

a-**Hydrazoximes.**—*Methyl-glyoxal-phenyl hydrazoxime*, $CH_3.C:N(NHC_6H_5).$-

CH : NOH, melting at 134°, is prepared by the action of phenylhydrazine upon isonitroso-acetoacetic acid. It parts readily with water and becomes methyl-n-phenyl osotriazole,



$$\begin{matrix} CH_3C = N \\ | \\ CH = N \end{matrix} > NC_6H_5$$

(A. 262, 278).

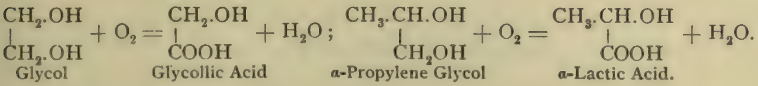
7. ALCOHOL- or OXY-ACIDS, $C_nH_{2n}<^{OH}_{CO_2H}$.

Acids of this series show a twofold character in their entire deportment. Since they contain a carboxyl group, they are *monobasic acids* with all the attaching properties and transpositions of the latter; the OH group linked to the radical bestows upon them all the properties of the *monohydric alcohols*. As already indicated in the introduction to the dihydric compounds, these alcohols must be distinguished as primary, secondary, and tertiary, according as they contain, in addition to the carboxyl group, the group $—CH_2OH$, characteristic of primary alcohols, the radical $=CHOH$, peculiar to the secondary alcohols, or the tertiary alcohol group $\equiv C . OH$. This difference manifests itself in the deportment of these bodies when subjected to oxidation. However, the manner in which the alcoholic hydroxyl group in an alcohol-acid acts upon the carboxyl group present in the same molecule depends greatly upon the position of these two groups with reference to each other. It is just this differentiating, opposing position of the two reactive groups which induces class differences of a distinctly new type, which are therefore made prominent because the oxidations manifested by primary, secondary and tertiary alcohols are already known to us. At present they are mostly termed *oxy-* or *hydroxy-fatty acids*, because of their origin from the fatty acids by the replacement of an hydrogen atom by OH.

The "Geneva names" are formed by the insertion of the syllable "ol," characteristic of alcohols, between the name of the hydrocarbon and the word acid: $CH_2OH . COOH$, oxyacetic acid, or [*ethanol acid*].

Glycollic and *ordinary* or *lactic acid of fermentation* are the best known and most important representatives.

General Methods of Formation.—(1) Careful oxidation (*a*) of diprimary, primary secondary and primary tertiary glycols with dilute nitric acid, or platinum sponge and air:



$$\underset{\text{Glycol}}{\begin{matrix} CH_2.OH \\ | \\ CH_2.OH \end{matrix}} + O_2 = \underset{\text{Glycollic Acid}}{\begin{matrix} CH_2.OH \\ | \\ COOH \end{matrix}} + H_2O ; \underset{\alpha\text{-Propylene Glycol}}{\begin{matrix} CH_3.CH.OH \\ | \\ CH_2OH \end{matrix}} + O_2 = \underset{\alpha\text{-Lactic Acid.}}{\begin{matrix} CH_3.CH.OH \\ | \\ COOH \end{matrix}} + H_2O.$$

(*b*) By the oxidation of oxyaldehydes.

(2) The action of nascent hydrogen (sodium amalgam, zinc and hydrochloric or sulphuric acid) upon the aldehyde acids, the ketonic

acids (pyroracemic acid, $CH_3 . CO . CO_2H$) and dicarboxylic acids (oxalic acid, $CO_2H . CO_2H$):

$$CH_3 . CO . CO_2H + 2H = CH_3 . CH(OH) . CO_2H$$
$$COOH . COOH + 4H = COOH . CH_2OH + H_2O.$$

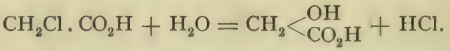
This reaction has been repeatedly used in preparing β-, γ- and δ-oxy-acids from β-, γ- and δ-ketone carboxylic esters.

(3) Some fatty acids have OH directly introduced into them. This is accomplished by oxidizing them with $KMnO_4$ in alkaline solution.

Only acids containing the tertiary group CH (a so-called tertiary H-atom) are adapted to this kind of transposition (R. Meyer, B. **11**, 1283, 1787; **12**, 2238; A. **208**, 60; **220**, 56). Nitric acid effects the same as MnO_4K (B. **14**, 1782; **16**, 2318).

(4) By heating unsaturated fatty acids with aqueous caustic potash or soda to 100° (A. **283**, 50).

(5) The transposition of the monohalogen fatty acids with silver oxide, boiling alkalies, or even water. The conditions of the reaction are perfectly similar to those observed in the conversion of the alkylogens into alcohols.



$$CH_2Cl . CO_2H + H_2O = CH_2{<}^{OH}_{CO_2H} + HCl.$$

The α-derivatives yield α-oxy-acids; the β-derivatives are occasionally changed to unsaturated acids by the splitting-off of a haloid acid, while the γ-compounds form γ-oxy-acids, which subsequently pass into lactones. γ-Halogen acids are converted directly into lactones by the alkaline carbonates.

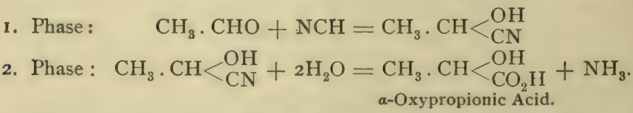
(6) By the action of nitrous acid upon amido-acids:

$$\underset{\text{Amido-acetic Acid}}{CH_2(NH_2) . CO_2H} + NO_2H = \underset{\text{Oxyacetic Acid.}}{CH_2(OH) . CO_2H} + N_2 + H_2O.$$

(7) The oxy-acids can be obtained from the diazo-fatty acids, on boiling them with water or dilute acids.

(8) From the α keton-alcohols—*e. g*, butyroïn and isovaleroïn (p. 317)—on treating them with alkalies and air.

Nucleus-synthetic Methods of Formation.—(9) By allowing hydrocyanic acid and hydrochloric acid to act upon the aldehydes and ketones. At first oxycyanides, the nitriles of oxy-acids (see these), are produced, after which hydrochloric acid changes the cyanogen group into carboxyl:



1. Phase: $CH_3 . CHO + NCH = CH_3 . CH{<}^{OH}_{CN}$

2. Phase: $CH_3 . CH{<}^{OH}_{CN} + 2H_2O = \underset{\alpha\text{-Oxypropionic Acid.}}{CH_3 . CH{<}^{OH}_{CO_2H}} + NH_3.$

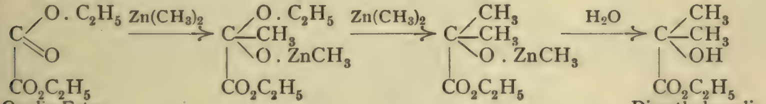
In preparing the oxycyanides, the aldehydes or ketones are treated with pure hydrocyanic acid, or we can add pulverized potassium cyanide to the ethereal solution of the ketone, and follow it with the gradual addition of concentrated hydrochloric acid (B. **14**, 1965; **15**, 2318). The concentrated hydrochloric acid changes the cyanides to acids, the amides of the acids being at first formed in the cold, but on boiling with more dilute acid they sustain further change to acids. Sometimes the change occurs more readily by heating with a little dilute sulphuric acid. Ethylene oxide behaves like acetaldehyde with prussic acid.

(10) The glycol chlorhydrins (p. 302) undergo a like alteration through the action of potassium cyanide and acids:

1. Phase: $CH_2.(OH).CH_2Cl + CNK = CH_2(OH).CH_2.CN + KCl$,
2. Phase: $CH_2.(OH).CH_2CN + 2H_2O = CH_2(OH).CH_2.CO_2H + NH_3$.

β-Oxypropionic Acid.

(11) A method of ready applicability in the synthesis of oxyacids consists in permitting zinc and alkyl iodides to act upon diethyl oxalic ester (Frankland and Duppa). This reaction is like that in the formation of tertiary alcohols from the acid chlorides by means of zinc ethyl, or of the secondary alcohols from formic esters (p. 114)—1 and 2 alkyl groups are introduced into one carboxyl group (A. **185**, 184):



Oxalic Ester

Dimethyl-oxalic Ester.

If we employ two alkyl iodides, two different alkyls may be introduced.

The acids obtained, as indicated, are named in accordance with their derivation from oxalic acid, but it would be more correct to view them as derivatives of oxyacetic acid or glycollic acid, $CH_2(OH).CO_2H$, and designate, *e.g.*, dimethyl-oxalic acid, as dimethyl-oxyacetic acid.

(12) When sodium or sodium ethylate acts upon the acetic esters and propionic esters it converts them into β-ketone carboxylic esters, but in the case of butyric and isobutyric esters it produces the ether esters of β-oxy-acids, such as *ethoxycaprylic ester*, $(CH_3)_2CH.CH(OC_2H_5).C(CH_3)_2.CO_2.C_2H_5$, from isobutyric ester (A. **249**, 54).

Reactions in which Groups are Split off.—(13) The fatty acids are formed from alkyl-malonic acids, $CRR'(CO_2R)_2$, by the withdrawal of a carboxyl group (p. 241), and the oxy-fatty acids are obtained in a similar manner from alkyl oxymalonic acids or tartronic acids:

$$CR(OH)<\genfrac{}{}{0pt}{}{CO_2H}{CO_2H} = CRH(OH).CO_2H + CO_2.$$

Alkyl-tartronic Acid Alkyl-oxy-acetic Acid.

The tartronic compounds are synthetically prepared from malonic acid esters, *e.g.*, $CH_2<\genfrac{}{}{0pt}{}{CO_2.C_2H_5}{CO_2.C_2H_5}$, by first introducing the alkyl group (see malonic acid), then replacing the second hydrogen of CH_2 by chlorine, and finally saponifying the alkylic monochlor-malonic ester with baryta (B. **14**, 619).

Isomerism.—The possible cases of isomerism with the oxy-acids are most simply deduced by considering the oxy-acids as the mono-hydroxyl substitution products of the fatty acids. Then the isomerides are the same as the mono-halogen fatty acids, which may be regarded as the haloid esters of the alcoholic acids corresponding to them.

Oxyacetic or glycollic acid is the only acid which can be obtained from acetic acid:

$CH_3 . COOH$	$CH_2OH . COOH$
Acetic Acid	Glycollic Acid (p. 334).

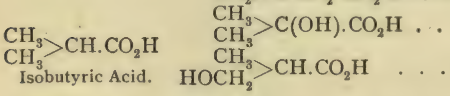
Propionic acid yields two oxypropionic acids:

$CH_3 . CH_2 . COOH$	$CH_3 . \overset{*}{C}H(OH) . COOH$	$CH_2(OH) . CH_2 . COOH$
Propionic Acid	α-Oxypropionic Acid ord. Lactic Acid (p. 335)	β-Oxypropionic Acid Hydracrylic Acid (p. 341).

These are distinguished as α- and β-oxypropionic acids respectively. The α-acid contains an asymmetric carbon atom. Theoretically, it should yield an inactive variety, which can be decomposed, and two optically active modifications. These, in fact, exist.

Normal butyric acid yields three and isobutyric acid two mono-carboxylic acids:

$CH_3.CH_2.CH_2CO_2H$ n-Butyric Acid	$CH_3.CH_2.CH(OH).CO_2H$	α-Oxybutyric Acid (p. 337)
	$CH_3.CH(OH).CH_2.CO_2H$	β-Oxybutyric Acid (p. 342)
	$CH_2OH.CH_2.CH_2.COOH$	γ-Oxybutyric Acid (p. 342)



$$\begin{array}{ll} {}^{CH_3}_{CH_3}{>}CH.CO_2H & {}^{CH_3}_{CH_3}{>}C(OH).CO_2H \\ \text{Isobutyric Acid.} & {}^{CH_3}_{HOCH_2}{>}CH.CO_2H \end{array}$$

. . . α-Oxyisobutyric Acid (p. 337)

. . . β-Oxyisobutyric Acid (unknown).

These alcohol-acids are themselves divided into—

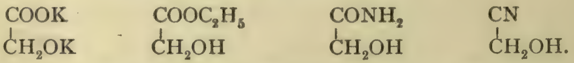
Primary acids: Glycollic acid, hydracrylic acid, γ-oxybutyric acid, β-oxyisobutyric acid.

Secondary acids: α-Oxypropionic acid, α-oxybutyric acid.

Tertiary acids: α-Oxyisobutyric acid.

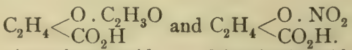
Properties.—The oxy-fatty acids containing one OH group are, in consequence, more readily soluble in water, and less soluble in ether than the parent acids (p. 245). They are less volatile and, as a general thing, can not be distilled without undergoing a change.

Deportment.—(1) The alcohol-acids behave like the mono-carboxylic acids, in that like these they yield, through a change in the carboxyl group, normal salts, esters, amides and nitriles:



$$\begin{array}{llll} COOK & COOC_2H_5 & CONH_2 & CN \\ | & | & | & | \\ CH_2OK & CH_2OH & CH_2OH & CH_2OH. \end{array}$$

(2) The remaining OH-group deports itself like that of the alcohols. Alkali metals and alkyls may replace its hydrogen. Acid radicals and NO_2 are substituted for it by the action of chlorides of monobasic acid radicals (like $C_2H_3O . Cl$), and a mixture of concentrated nitric and sulphuric acids:

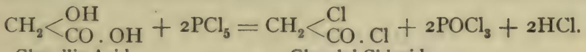


$$C_2H_4{<}^{O . C_2H_3O}_{CO_2H} \text{ and } C_2H_4{<}^{O . NO_2}_{CO_2H.}$$

Aceto-lactic Acid Nitro-lactic Acid.

Both of these reactions are characteristic of the hydroxyl groups of the alcohols (p. 303).

(3) PCl_5 replaces the two hydroxyl groups by chlorine:



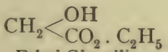
$$CH_2{<}\begin{matrix}OH\\CO\,.\,OH\end{matrix} + 2PCl_5 = CH_2{<}\begin{matrix}Cl\\CO\,.\,Cl\end{matrix} + 2POCl_3 + 2HCl.$$

Glycollic Acid

Glycolyl Chloride, or
Chloracetyl Chloride.

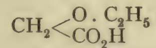
The acid chlorides corresponding to the oxy-acids are not known. Instead of these we get the chlorides of the corresponding monochlor fatty acids, in which the chlorine in union with CO is very reactive with water and alcohols, yielding free acids and their esters; in the case cited, monochlor-acetic acid, $CH_2Cl\,.\,CO_2H$, and its esters result. The remaining chlorine atom is, on the contrary, more firmly united, as in ethyl chloride.

In addition to ethyl glycollic ester there are ethyl glycollic acid and ethyl etho-glycollic ester:



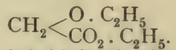
$$CH_2{<}\begin{matrix}OH\\CO_2\,.\,C_2H_5\end{matrix}$$

Ethyl Glycollic
Ester



$$CH_2{<}\begin{matrix}O\,.\,C_2H_5\\CO_2H\end{matrix}$$

Ethyl Glycollic
Acid



$$CH_2{<}\begin{matrix}O\,.\,C_2H_5\\CO_2\,.\,C_2H_5.\end{matrix}$$

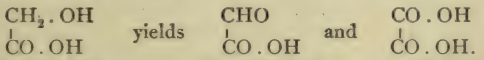
Ethyl Etho-glycollic
Ester.

Alkalies cause the alkyl combined with CO_2 to separate, forming ethyl glycollic acid.

(4) The oxy-acids are reduced to their corresponding fatty acids (p. 240) when they are heated with hydriodic acid.

(5) While in the preceding transpositions all the oxy-acids react similarly, the primary, secondary and tertiary alcohol acids show marked differences when they are oxidized.

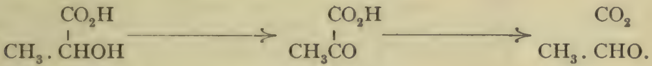
(*a*) The *primary* oxy-acids yield, by oxidation, aldehyde acids:



$$\begin{matrix}CH_2\,.\,OH\\|\\CO\,.\,OH\end{matrix}\ \text{yields}\ \begin{matrix}CHO\\|\\CO\,.\,OH\end{matrix}\ \text{and}\ \begin{matrix}CO\,.\,OH\\|\\CO\,.\,OH.\end{matrix}$$

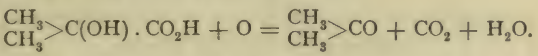
Glycollic Acid Glyoxylic Acid Oxalic Acid.

(*b*) The *secondary* oxy-acids yield ketonic acids: the α-ketonic acids change to aldehyde and CO_2, the β-ketonic acids to ketones and CO_2:



$$\begin{matrix}CO_2H\\|\\CH_3\,.\,CHOH\end{matrix} \longrightarrow \begin{matrix}CO_2H\\|\\CH_3CO\end{matrix} \longrightarrow \begin{matrix}CO_2\\ \\CH_3\,.\,CHO.\end{matrix}$$

(*c*) Tertiary α-oxy-acids yield ketones:



$$\begin{matrix}CH_3\\CH_3\end{matrix}{>}C(OH)\,.\,CO_2H + O = \begin{matrix}CH_3\\CH_3\end{matrix}{>}CO + CO_2 + H_2O.$$

(6) The α-oxy-acids undergo a like decomposition when heated with dilute sulphuric or hydrochloric acid (or by action of concentrated H_2SO_4). Their carboxyl group is removed as formic acid (when concentrated H_2SO_4 is employed, CO and H_2O are the products):

$$(CH_3)_2C(OH)\,.\,CO_2H = (CH_3)_2CO + HCO_2H$$
$$CH_3\,.\,CH(OH)\,.\,CO_2H = CH_3\,.\,CHO + HCO_2H.$$

Another alteration is sustained by the α-oxy-acids at the same time; it, however, does not extend far. Water is eliminated and unsaturated acids are produced. This change is easily effected when PCl_3 is allowed to act on the esters of *a*-oxy-acids (p. 277).

(7) Especially interesting is the deportment of the *a*-, *β*-, *γ*,- or *δ* oxy-acids in respect to the exit of water from carboxyl and alcoholic hydroxyl groups.

(*a*) The *a-oxy-acids* lose water when they are heated and become *cyclic double esters*—the *lactides*—in the formation of which two molecules of the *a*-oxy-acid have taken part:

$$\begin{array}{c}\text{COOH}\\ |\\ \text{CH}_3\text{CHOH}\end{array} + \begin{array}{c}\text{HO.CH.CH}_3\\ |\\ \text{HOCO}\end{array} = \begin{array}{c}\text{CO.O.CH.CH}_3\\ |\qquad\quad |\\ \text{CH}_3\text{CHO}-\text{CO}\end{array} + 2H_2O.$$

a-Oxypropionic Acid or Lactic Acid Lactide.

(*b*) When the *β-oxy-acids* are heated alone, water is withdrawn and unsaturated acids are the products (p. 277):

$$\underset{\substack{\beta\text{-Oxypropionic Acid}\\ \text{Hydracrylic Acid}}}{CH_2(OH).CH_2.CO_2H} = \underset{\text{Acrylic Acid.}}{CH_2:CH.CO_2H} + H_2O.$$

(*c*) The *γ*- and *δ-oxy-acids* lose water at the ordinary temperature, and change more or less completely into simple *cyclic esters*—the *γ*- and *δ*-lactones.

The *a*-, *β*-, *γ*- and *δ*-amido-carboxylic acids corresponding to the *a*-, *β*-, *γ*-, and *δ*-oxy-acids show differences similar to those manifested by the latter.

STRUCTURE OF NORMAL CARBON CHAINS AND THE FORMATION OF LACTONES.

The peculiar differences in the deportment of the *a*-, *β*-, *γ*- and *δ*-oxy-acids when they split off water have contributed to the development of a representation of the spacial arrangement or configuration of carbon chains (B. 15, 630). The assumption that the atoms of a molecule not linked to each other in a formula can exert an affinity upon one another has led to the idea that, in a union of more than two C atoms, these atoms arrange themselves not in a straight line, but upon a curve. We can then comprehend that cyclic, simple ester formation can not take place between the first and second carbon atoms, rarely between the second and third (in aromatic oxy-acids), and readily between the first and fourth or first and fifth carbon atoms, which have approached so near to each other that an oxygen atom is capable of bringing about a closed ring (see ethylene oxide, p. 298, and tri-methylene oxide, p. 299, as well as the strain theory of v. Baeyer in the introduction to the carbocyclic derivatives).

A. SATURATED OXYMONO-CARBOXYLIC ACIDS, OXYPARAFFIN MONO-CARBOXYLIC ACIDS, *a*-OXY-ACIDS.

(1) **Glycollic Acid,** Oxy-acetic Acid [Ethanol Acid], $CH_2.OH.COOH$, melting at 80°, occurs in unripe grapes and in the leaves of *Ampelopsis hederacea.*

History.—Glycollic acid was first obtained in 1848 by Strecker from amidoacetic acid or glycocoll—hence the name—according to the sixth method of formation (p. 330). In 1856 Debus discovered it together with glyoxal and glyoxylic acid among the oxidation products obtained from ethyl alcohol by the action of nitric acid. Würtz in 1857 observed its formation in the oxidation of *ethylene glycol*, and Kekulé in 1858 showed how it could be made by boiling a solution of potassium chloracetate (A. **105**, 286; compare B. **16**, 2414; A. **200**, 75; B. **26**, R. 606).

It is also produced by the action of caustic potash (p. 320) on *glyoxal*, by the reduction of *oxalic acid* (second method of formation, p. 329), and from *diazoacetic ester* by the seventh method of formation. Its nitrile results when prussic acid acts upon *formaldehyde* (ninth method), and is converted by hydrochloric acid into glycollic acid. It also appears in the oxidation of glycerol and glucoses by silver oxide.

Glycollic acid crystallizes from acetone. It is very soluble in water and alcohol. Diglycollide and polyglycollide (p. 339) are produced when it is heated. Nitric acid oxidizes it to oxalic acid.

Calcium Salt, $(CH_2OHCO_2)_2Ca+3H_2O$. *Ethyl Ester*, $CH_2OH.CO_2C_2H_5$, boils at 160°.

(2) **Lactic Acid of Fermentation**, *α*-Oxypropionic Acid, Ethidene Lactic Acid, [d+l] Lactic Acid [2-Propanol Acid], $CH_3CH(OH)CO_2H$; melting at 18° and boiling at 120° (12 mm.) (B. **28**, 2597), is isomeric with *β-oxypropionic acid, hydracrylic acid*, or [3-*propanol acid*] $CH_2OH.CH_2CO_2H$, which will be discussed later as the first *β*-oxy-acid.

Lactic Acid is formed by a peculiar fermentation, the lactic acid fermentation of milk-sugar, cane-sugar, gum and starch. It is, therefore, contained in many substances which have soured,—*e. g.*, in sour milk, in sour-kraut, pickles, also in the gastric juice.

Methods of Formation.—The acid is artificially prepared by the methods already described: (1) from *α* propylene glycol; (2) from pyroracemic acid; (5) from *α*-chlor- or brom-propionic acid; (6) from alanine; (9) from acetaldehyde and prussic acid; (13) by heating isomalic acid, $CH_3C(OH)(COOH)_2$ (B. **26**, R. 7).

Other methods consist in heating grape-sugar and cane-sugar with water and 2–3 parts barium hydrate to 160°, and *α*-dichloracetone, $CH_3.CO.CHCl_2$, with water to 200°.

Lactic Acid Fermentation.—This fermentation is induced in sugar solutions by a peculiar ferment, the lactic acid bacillus, which is present in decaying cheese. It proceeds most rapidly at temperatures ranging from 35–45°. It is noteworthy that the bacillus alluded to is very sensitive to free acid. The fermentation is arrested when sufficient lactic acid is produced, but is again renewed when the acid is neutralized. Therefore, zinc or calcium carbonate is added at the very beginning, and the lactic acid thus obtained, either as the calcium or zinc salt. Should the fermentation continue for some time the lactic will pass into butyric fermentation, the insoluble calcium lactate will disappear, and the solution will at last contain calcium butyrate (compare n-butyric acid, p. 247).

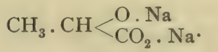
History.—Scheele discovered (1780) lactic acid in sour milk. In 1847 Liebig demonstrated that the sarcolactic acid found by Berzelius (1808) in the juices of the muscles was different from the lactic acid of fermentation. Würtz (1858) described the formation of fermentation lactic acid from *α*-propylene glycol and air in the presence of platinum black, and recognized that it was a dibasic acid. Kolbe (1859) obtained lactyl chloride by the action of PCl_5 upon calcium lactate. This body is identical with chlorpropionyl chloride, and lactic acid is therefore monobasic and must be considered as oxypropionic acid. Later (1860) Würtz called it a diatomic, monobasic acid, meaning to indicate thereby that one of the two typical hydrogen atoms is more basic than the other. The declaration of Kekulé that lactic acid is both an acid and an alcohol (B. **20**, R. 948) is more to the point. Strecker was the first to synthesize the acid from synthetic amido-lactic acid or alanine, which had also been prepared by him through the interaction of prussic acid and aldehyde ammonia.

Fermentation lactic acid is a syrup soluble in water, alcohol and ether. It is optically inactive. Placed in a desiccator over sulphuric acid, it partially decomposes into water and its anhydride. When distilled it yields lactide, aldehyde, carbon monoxide and water.

Heated to 130° with dilute sulphuric acid, it decomposes into aldehyde and formic acid; when oxidized with $KMnO_4$ it yields pyroracemic acid, while with chromic acid acetic acid and carbon dioxide are formed. Heated with hydrobromic acid, it changes to *a* brompropionic acid.

Hydriodic acid at once reduces it to propionic acid, and PCl_5 changes it into chlorpropionyl chloride.

Lactates.—The *sodium salt*, $C_3H_5O_3Na$, is an amorphous mass. When heated with metallic sodium, we get the *disodium compound*:



$$CH_3.CH\begin{cases}O.Na\\CO_2.Na\end{cases}$$

The *calcium salt*, $(C_3H_5O_3)_2Ca + 5H_2O$, is soluble in ten parts of cold water, and is very readily dissolved by hot water.

The *zinc salt*, $(C_3H_5O_3)_2Zn + 3H_2O$, dissolves in 58 parts of cold and 6 parts hot water. The *iron salt*, $(C_3H_5O_3)_2 Fe + 3H_2O$.

The Optically Active Lactic Acids.

The optically inactive, fermentation lactic acid contains an asymmetric carbon atom indicated in the formula $CH_3.\overset{*}{C}H.OH.CO_2H$ by the small star. The acid can be resolved by strychnine into two optically active components,—dextrolactic acid and lævolactic acid,—with similar but opposite rotatory power. The strychnine salt of the lævo-acid crystallizes out first (B. **25**, R. 794). Therefore, in the following pages those substances will be called optically inactive which can be resolved into or formed from two optically active isomerides, called [*d* + *l*] modifications. On mixing solutions of equal quantities of lævo- and dextro-lactate of zinc, the zinc salt of fermentation lactic acid will be produced, and, being more insoluble, will crystallize out. The dextro- modification will remain, if *Penicillium glaucum* is permitted to grow in the solution of inactive ammonium lactate (B. **16**, 2720). The lævo-rotatory modification is produced in the breaking down of a cane-sugar solution by *Bacillus acidi lævolactici* (B. **24**, R. 150).

Sarcolactic Acid, *Dextrolactic Acid*, *Paralactic Acid*, discovered in 1808 by Berzelius in the juice of the muscles, and shown by Liebig (1848) to be different from the lactic acid of fermentation, is present in different animal organs. It is most conveniently obtained from Liebig's beef-extract.

Dextro- and lævo-lactates of zinc crystallize with two molecules of water—$(C_3H_5O_3)_2Zn + 2H_2O$. For other salts consult B. **29**, R. 899.

Homologous α-Oxy-acids.—The homologous α-oxy-acids are, from the very nature of things, either secondary or tertiary alcohol acids. Glycollic acid is the only primary α-alcohol acid. (*a*) The *secondary alcohol acids* are generally formed (1) from the corresponding α-halogen fatty acids (method 5); (2) *nucleus-synthetic*, from aldehydes and prussic acid, and subsequent saponification of the nitriles of the oxy-acids by means of hydrochloric acid (method 9). (*b*) The *tertiary oxy-acids* result

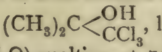
(1) From the oxidation of dialkyl-acetic acid (general method 3).

(2) Upon treating α-ketone alcohols with alkalies and air (method 8, p. 330).

(3) By the action of prussic acid and hydrochloric acid upon ketones (method 9).

(4) When zinc and alkyl iodides react with oxalic ester (method 11, p. 331).

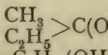
Oxybutyric Acids.—Four of the five possible isomerides are known; two of these are α-oxy-acids: (1) *α-Oxybutyric Acid*, $CH_3 . CH_2 . CH(OH)CO_2H$, melting at 43°, has been resolved by brucine into its optically active components (B. **28**, R. 278, 325, 725). (2) *α-Oxyisobutyric Acid*, Butyl-lactinic Acid, Acetonic Acid, Dimethyl-oxalic Acid [2-Methyl-2-propanol Acid], $(CH_3)_2C(OH)COOH$, melting at 79° and boiling at 212°, is obtained from dimethyl-acetic acid, from acetone and from oxalic ester (see above); hence the names acetonic acid and dimethyl-oxalic acid. It is produced when β-isoamylene glycol is oxidized by nitric acid, and is obtained from α-brom- and α-amidobutyric acid, as well as from acetone chloroform.

Acetone Chloroform,  $(CH_3)_2C{<}\begin{smallmatrix}OH\\CCl_3\end{smallmatrix}$, liquid modification, boiling at 170°, the solid modification $(+1\frac{1}{2}H_2O)$ melting at 79° and boiling at 167°, is a remarkable derivative of α-oxyisobutyric acid. It is the chloride of ortho-α-oxyisobutyric acid (p. 224), which bears the same relation to α-oxyisobutyric acid as chloroform to formic acid. It is converted by aqueous alkalies into α-oxyisobutyric acid. By the action of chloroform and caustic potash the liquid modification is first produced, which takes up water in moist air and changes to the solid variety (Willgerodt, B. **20**, 2445; **29**, R. 908).

α-Oxyvaleric Acids:

α-Oxy-n-valeric Acid, $CH_3 . CH_2 . CH_2 . CH(OH) . CO_2H$, melts at 28–29° (B. **18**, R. 79).

α-Oxyisovaleric Acid, $(CH_3)_2 . CH . CH(OH) . CO_2H$, melts at 86° (A. **205**, 28; B. **28**, 296).

Methyl-ethyl Glycollic Acid,  $\begin{smallmatrix}CH_3\\C_2H_5\end{smallmatrix}{>}C(OH) . CO_2H$ (A. **204**, 18).

Oxycaproic Acids, $C_6H_{12}O_3 = C_5H_{10}(OH) . CO_2H$.

α-Oxycaproic Acid, $CH_3 . (CH_2)_3 . CH(OH) . CO_2H$, is probably the so-called **leucic acid**, obtained from leucine by the action of nitrous acid. It melts at 73° (Strecker, 1848).

α-Oxyisobutyl-acetic Acid, $(CH_3)_2CH . CH_2CH(OH)CO_2H$, melting at 54°, is obtained from inactive α-amidoisobutyl-acetic acid, or isoleucine (B. **26**, 56). *α-Oxydiethyl-acetic Acid*, Diethyl-oxalic Acid, $(C_2H_5)_2C(OH)CO_2H$, melts at 80° (A. **200**, 21). *α-Oxytertiary-butyl-acetic Acid*, $(CH_3)_3C . CH(OH)CO_2H$, by the reduction of trimethyl-pyroracemic acid, melts at 87° (see this).

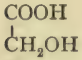
α-Oxycaprylic Acids, *α-Oxy-n-caprylic Acid*, $CH_3(CH_2)_5CH(OH)CO_2H$, from œnanthol, melts at 69.5°. *Di-n-propyl Glycollic Acid*, *α-Oxy-di-n-propyl-acetic Acid*, $(C_3H_7)_2C(OH).CO_2H$, from butyroin (p. 317), melts at 72° (B. **24**, 1273). *Di-isopropyl Oxalic Acid*, α-Oxy-di-isopropyl-acetic Acid, $(C_3H_7)_2C(OH)CO_2H$, melts at 111° (B. **28**, 2463). *Di-isobutyl Glycollic Acid* $(C_4H_9)_2C(OH)CO_2H$, melts at 114°.

α-Brom-fatty acids have yielded the following: α-oxymyristic acid, $C_{13}H_{26}(OH).CO_2H$, melting at 51° (B. **22**, 1747); *α-Oxypalmitic Acid*, $C_{15}H_{30}(OH)CO_2H$, melting at 82° (B. **24**, 939); *α-Oxystearic Acid*, $C_{17}H_{34}(OH)CO_2H$, melting at 84–86° (B. **24**, 2388).

In the following pages those α-oxy-acid derivatives will be described which belong to glycollic and lactic acids.

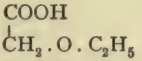
Alkyl Derivatives of the α-Oxy-acids.

A single α-oxy-acid yields three kinds of alkyl derivatives: *ethers*, *esters* and *ether-esters*:



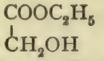
$$\begin{array}{l} COOH \\ | \\ CH_2OH \end{array}$$

Glycollic Acid



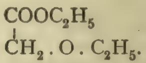
$$\begin{array}{l} COOH \\ | \\ CH_2.O.C_2H_5 \end{array}$$

Ethyl Glycollic Acid



$$\begin{array}{l} COOC_2H_5 \\ | \\ CH_2OH \end{array}$$

Glycollic Ethyl Ester



$$\begin{array}{l} COOC_2H_5 \\ | \\ CH_2.O.C_2H_5. \end{array}$$

Ethyl Glycollic Ethyl Ester.

(1) The *alkyl ethers* of the α-oxy-acids are obtained (1) by the action of sodium alcoholates upon salts of the α-halogen substitution products of the fatty acids; (2) by the saponification of the dialkyl-ether esters of the α-oxy-acids.

Methyl-ether Glycollic Acid, $CH_3OCH_2 \cdot COOH$, boils at 198°. *Ethyl Glycollic Acid* boils at 206–207°. *α-Ethoxyl-propionic Acid*, $CH_3CH(OC_2H_5).CO_2H$, boils with partial decomposition from 195–198°.

(2) *Alkyl Esters* of the α-oxy-acids result (1) on heating the free acids with absolute alcohol; (2) when the cyclic double esters, the lactides, are heated with alcohols. *Glycollic Methyl Ester*, $CH_2(OH)COOCH_3$, boils at 151°. *Glycollic Ethyl Ester* boils at 160°. *Lactic Methyl Ester*, $CH_3CH(OH)CO_2CH_3$, boils at 145°. *Lactic Ethyl Ester* boils at 154.5°.

(3) The *dialkyl-ether esters* of the α-oxy-acids are produced (1) when sodium alcoholates act upon the esters of α-halogen fatty acids; (2) by the interaction of alkylogens and the sodium derivatives of the alkyl esters of the α-oxy-acids.

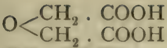
Methyl Glycollic Methyl Ester, $CH_2(OCH_3).COOCH_3$, boils at 127°.

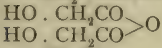
Ethyl Ester boils at 131°.

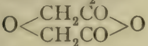
Ethyl Glycollic Methyl Ester, $CH_2(O.C_2H_5)CO.OCH_3$, boils at 148°. *Ethyl Glycollic Ethyl Ester* boils at 152° (B. **17**, 486). *Methyl Lactic Methyl Ester*, $CH_3CH(OCH_3)COOCH_3$, boils at 135–138°. *Ethyl ester* boils at 135.5°. *Ethyl Lactic Ethyl Ester*, $CH_3.CH(OC_2H_5).COOC_2H_5$, boils at 155° (A. **197**, 21).

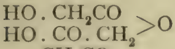
Anhydride Formation of the α-Oxy-acids.

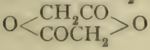
The ethers of the alcohols may be considered as their anhydrides, for they sustain the same relation to the alcohols as the anhydrides of the mono-carboxylic acids bear to the latter. When in the anhydride formation one molecule of an alcohol and a molecule of a carboxylic acid combine, the product is an *ester*. As the α-alcohol acids exhibit both the character of a carboxylic acid and that of an alcohol, it is possible to have all these varieties of anhydride formations occurring with an α-oxy-acid. Glycollic acid has been most thoroughly studied in this direction.

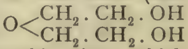
1.  $O<\begin{matrix}CH_2\cdot COOH\\CH_2\cdot COOH\end{matrix}$ Alcohol anhydride of glycollic acid : *Diglycollic Acid.*

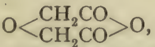
2.  $\begin{matrix}HO\cdot CH_2CO\\HO\cdot CH_2CO\end{matrix}>O$ Glycollic anhydride is not known.

3.  $O<\begin{matrix}CH_2CO\\CH_2CO\end{matrix}>O$ Alcohol- and acid-anhydride of glycollic acid: *Diglycollic Anhydride.*

4.  $\begin{matrix}HO\cdot CH_2CO\\HO\cdot CO\cdot CH_2\end{matrix}>O$ Open ester acid : *Glycollo-glycollic Acid.*

5.  $O<\begin{matrix}CH_2CO\\COCH_2\end{matrix}>O$ Closed, cyclic double ester of glycollic acid : *Glycollide,* simplest *Lactide.*

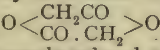
Diglycollic Acid, $C_4H_6O_5$, the alcohol anhydride of glycollic acid is formed on boiling monochloracetic acid with lime, baryta, magnesia, or lead oxide (also with glycollic acid), and in the oxidation of diethylene glycol,  $O<\begin{matrix}CH_2\cdot CH_2\cdot OH\\CH_2\cdot CH_2\cdot OH\end{matrix}$ (p. 295). Diglycollic acid crystallizes with water in large rhombic prisms, which melt at 148°.

Diglycollic Anhydride,  $O<\begin{matrix}CH_2CO\\CH_2CO\end{matrix}>O$, melting at 97° and boiling at 240°, is isomeric with glycollide. It is obtained from glycollic acid by a simultaneous alcohol-anhydride and acid-anhydride formation. It also results upon heating diglycollic acid, or by boiling it with acetyl chloride (A. **273**, 64).

Dilactylic Acid, $O(CH_3\cdot CH\cdot COOH)_2$, has received little attention.

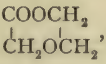
Glycollo-gycollic Acid, $CH_2(OH).COOCH_2COOH$, generally termed glycollic anhydride, and *Lactylolactic Acid,* $CH_3CH(OH)COOCH(CH_3)COOH$, commonly called lactic anhydride, have not been well studied. They are produced when the free α-oxyacids are heated to 100°. They constitute intermediate steps in the lactide formation (B. **23**, R. 325).

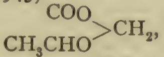
Lactides: Cyclic Double Esters of the α-Oxyacids.

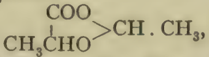
Diglycollide,  $O<\begin{matrix}CH_2CO\\CO\cdot CH_2\end{matrix}>O$, melting at 86°, is produced when polyglycollide is distilled under greatly reduced pressure. When heated at the ordinary pressure, or if preserved, it reverts to polyglycollide, from which it differs by its lower melting point and ready solubility in chloroform. It combines readily with water (A. **279**, 45).

Polyglycollide, $(C_2H_2O_2)x$, melting at 223°, is formed on heating glycollic acid, and when dry sodium chloracetate is heated alone to 150°. It passes into glycollic esters when heated with alcohols in sealed tubes (A. **279**, 45).

Lactide,  $O<\begin{matrix}CH(CH_3)CO\\COCH(CH_3)\end{matrix}>O$, melting at 125°, boiling at 255° (760 mm.), 138° (12 mm.) (B. **28**, 2595), results on heating lactic acid under diminished pressure. It can be recrystallized from chloroform (A. **167**, 318; B. **25**, 3511). See B. **26**, 263; A. **279**, 100, for homologous lactides.

Cyclic Ether Esters.—*Glycollic Ethylene Ester,*  $\begin{matrix}COOCH_2\\ | \qquad | \\ CH_2OCH_2\end{matrix}$, melts at 31°, and boils at 214° (B. **27**, 2945).

Methylene Lactate,  $\begin{matrix}COO\\CH_3CHO\end{matrix}>CH_2$, boils at 153° (B. **28**, R. 180).

Lactic Ethidene Ester,  $\begin{matrix}COO\\ | \\ CH_3CHO\end{matrix}>CH\cdot CH_3$, boiling at 151°, is produced when lactic acid and acetaldehyde are heated to 160°. Its hexachlor-derivative is chloralide (p. 340).

Acid Esters of the α-Oxyacids (pp. 144, 300).

Nitric Lactic Ester, Nitrolactic acid, $CH_3\cdot CHO(NO_2)\cdot COOH$, is a yellow liquid, decomposing at the ordinary temperature into oxalic and prussic acids (B. **12**, 1837).

Acetyl Glycollic Acid, $CH_2O(COCH_3)COOH$, is obtained from glycollic acid and acetic anhydride. The *ethyl ester*, $CH_2O(COCH_3)COOC_2H_5$, boils at 179°. *Acetyl Lactic Acid*, $CH_3CH(OCOCH_3)COOH$, is present in *beef extract* (B. **22**, 2713). The *ethyl ester*, $CH_3 . CH(OCOCH_3)COOC_2H_5$, boils at 177°.

Halogen α-Oxyacids.

β-Monohalogen Ethidene Lactic Acids.—*β-Chlorlactic Acid*, $CH_2Cl . CH(OH) . CO_2H$, melts at 78°. *β-Bromlactic Acid*, $CH_2Br . CHOH . CO_2H$, melts at 89°. *β-Iodolactic Acid*, $CH_2I . CH(OH)CO_2H$, melts at 100°. These three acids have been prepared by adding hydrogen chloride, bromide or iodide to epihydrinic or glycidic acid, $\overline{CH_2CH(O})CO_2H$.

β-Chlorlactic acid is also formed from monochloraldehyde by the action of hydrocyanic acid and by the oxidation of epichlorhydrin, $\overline{CH_2CH(O})CH_2Cl$, and α-chlorhydrin, $CH_2Cl . CH(OH) . CH_2 . OH$, with concentrated HNO_3; as well as by the addition of hypochlorous acid to acrylic acid (together with α-chlorhydracrylic acid).

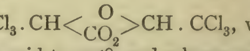
Silver oxide converts it into glyceric acid; when reduced with hydriodic acid it becomes β-iodpropionic acid. Heated with alcoholic potash it is again changed to epihydrinic acid (see above), just as ethylene oxide is obtained from glycolchlorhydrin (p. 298).

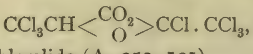
Higher halogen substitution products of the α-oxyacids have been prepared by the gradual treatment of halogen aldehydes, like dichloraldehyde, chloral, bromal, and trichlorbutyric aldehyde with hydrocyanic acid and hydrochloric acid. Trichlorlactic acid has been the most thoroughly studied.

β-Dichlorlactic Acid, $CHCl_2 . CH(OH) . CO_2H$, melts at 77°.

β-Trichlorlactic Acid, $CCl_3 . CH(OH) . CO_2H$, melts at 105°–110°, and is soluble in water, alcohol and ether. Alkalies easily change it to chloral, chloroform and formic acid. Zinc and hydrochloric acid reduce it to dichlor- and mono-chloracrylic acids (p. 281). Its ethyl ester melts at 66°–67°, and boils at 235°. The best method of preparing it consists in heating chloralcyanhydrin with alcohol and sulphuric acid or HCl (B. **18**, 754).

Because trichlorlactic acid yields chloral without difficulty, it is converted quite readily, by different reactions, into derivatives of chloral and glyoxal. It forms glyoximes with hydroxylamine, and glycosin with ammonia (p. 321, and B. **17**, 1997).

Chloralide, *Trichlorethidene-trichlorlactic Ester*,  $CCl_3 . CH\langle{}^{O}_{CO_2}\rangle CH . CCl_3$, was first prepared by heating chloral with fuming sulphuric acid to 105°, and subsequently when trichlorlactic acid was heated to 150° with excess of chloral. It melts at 114° and boils at 272°. When heated to 140° with alcohol, it breaks up into trichlorlactic ester and chloral alcoholate (Wallach, A. **193**, 1). Chloral also unites with lactic and other oxyacids, like glycollic, malic, salicylic, etc., forming the so-called *chloralides* (A. **193**, 1).

Perchlorethidene-trichlorlactic Ester,  $CCl_3CH\langle{}^{CO_2}_{O}\rangle CCl . CCl_3$, boiling at 276°, is obtained by the action of PCl_5 upon chloralide (A. **253**, 121).

Tribromlactic Acid, $CBr_3 . CH(OH) . CO_2H$, melts at 141°–143° and unites with chloral and bromal to corresponding chloralides and bromalides.

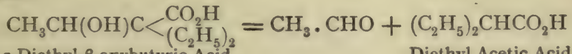
Trichlorvalerolactinic Acid, $CH_3 . CCl_2 . CHCl . CH(OH) . CO_2H$, melts at 140° (A. 179 99).

β-Oxycarboxylic Acids.

Generally the β-oxycarboxylic acids, when heated, part with water and become unsaturated olefine carboxylic acids:

$$\underset{\text{Ethylene Lactic Acid or Hydracrylic Acid}}{CH_2OH . CH_2 . CO_2H} \xrightarrow{-H_2O} \underset{\text{Acrylic Acid.}}{CH_2 = CHCO_2H}$$

In the case of the higher homologues of ethylene lactic acid, when water is eliminated, both αβ- and βγ-olefine carboxylic acids (B. **26**, 2079) result. The *α-dialkyl-β oxybutyric acids*, resulting from the reduction of dialkyl acetoacetic esters, decompose with difficulty on the application of heat: the products being *aldehyde* and *dialkyl acetic acids:*

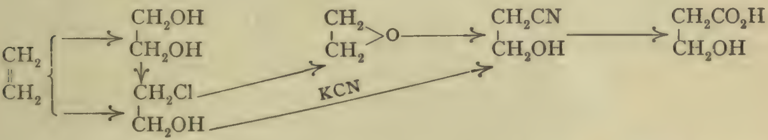


$$CH_3CH(OH)C{<}{}^{CO_2H}_{(C_2H_5)_2} = CH_3 . CHO + (C_2H_5)_2CHCO_2H$$

α-Diethyl-β-oxybutyric Acid Diethyl Acetic Acid.

β-Oxyacids are produced (method **1**) in the oxidation of primary-secondary and primary-tertiary glycols; (method 2) (p. 329) by the reduction of β-ketone carboxylic esters (secondary oxyacids), and (method 3) on boiling βγ- or Δ_2-olefine carboxylic acids with caustic soda. Furthermore, zinc and the esters of the monohalogen fatty acids—*e. g.*, bromisobutyric ester—combine with aldehydes (isobutyl aldehyde) to form secondary β-oxyacids, and with ketones to form tertiary β-oxyacids (B. **28**, 2838, 2842).

Ethylene Lactic Acid, Hydracrylic Acid [3-Propanol Acid], $CH_2(OH).CH_2.CO_2H$, is isomeric with *ethidene lactic acid* or the lactic *acid of fermentation*, and is obtained (1) by the oxidation of trimethylene glycol; (2) from β-iodpropionic acid, or β-chlorpropionic acid, with moist silver oxide; (3) from acrylic acid by heating with aqueous sodium hydroxide to 100°; (4) by the saponification of ethylene cyanhydrin with hydrochloric acid. This reaction completes the synthesis of ethylene lactic acid from ethylene:

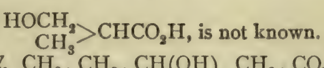


The free acid yields a non-crystallizable, thick syrup. When heated alone, or when boiled with sulphuric acid (diluted with 1 part H_2O), it loses water and forms acrylic acid (hence the name hydracrylic acid.

Hydriodic acid again changes it to β-iodpropionic acid. It yields oxalic acid and carbon dioxide when oxidized with chromic acid or nitric acid.

The *sodium salt*, $C_3H_5O_3Na$, melting at 142–143°, and the *calcium salt*, $(C_3H_5O_3)_2$-$Ca + 2H_2O$, fusing at 140–145°, when heated above their melting points pass into the corresponding acrylates. The *zinc salt*, $(C_3H_5O_3)_2Zn + 4H_2O$, is soluble in water and alcohol, whereas the latter precipitates zinc α-lactate and paralactate.

β-**Oxybutyric Acid** [3-Butanol Acid], $CH_3 . \overset{*}{C}H(OH) . CH_2 . CO_2H$ (compare p. 332 for the isomerism), is formed by the action of sodium amalgam upon acetoacetic ester (see this), by the oxidation of aldol (p. 321) with silver oxide, and from α-propylene chlorhydrin, $CH_3 . CH(OH) . CH_2Cl$, by the action of CNK and subsequent saponification of the cyanide. It is a thick, non-crystallizable syrup, which volatilizes with steam. When heated the acid decomposes (like all β-oxy-acids, p. 334) into water and crotonic acid, $CH_3 . CH : CH . CO_2H$. An optically active β-oxybutyric acid has been isolated from diabetic urine (B. **18**, R. 451).



β-Oxyisobutyric Acid, $\begin{matrix}HOCH_2\\CH_3\end{matrix}\!>CHCO_2H$, is not known.

β-Oxy-n-valeric Acid, $CH_3 . CH_2 . CH(OH) . CH_2 . CO_2H$ (A. **283**, 74, 94). *α-Methyl-β-oxybutyric Acid*, $CH_3 . CH(OH) . CH(CH_3) . CO_2H$ (A. **250**, 244). *β-Oxyisovaleric Acid*, $(CH_3)_2C(OH)CH_2 . CO_2H$, results when isobutyl formic acid is oxidized with $KMnO_4$ (A. **200**, 273).

β-Oxy-n-Caproic Acid, $CH_3 . CH_2 . CH_2 . CH(OH)CH_2CO_2H$, is formed on boiling hydrosorbic acid with caustic soda (A. **283**, 124). *α-Ethyl-β-oxybutyric Acid*, $CH_3 . CH(OH) . CH(C_2H_5) . CO_2H$ (A. **188**, 240). *α-Methyl-β-oxyvaleric Acid*, $CH_3 . CH_2CH(OH)CH(CH_3) . CO_2H$ (B. **20**, 1321).

β-Oxyisocaproic Acid, $(CH_3)_2CH . CH(OH) . CH_2 . CO_2H$ (B. **29**, R. 667).

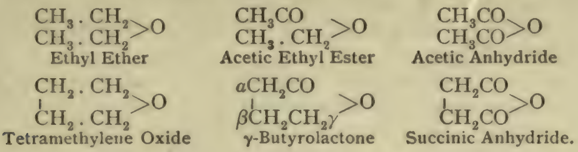
β-Oxyisoheptylic Acid, $(CH_3)_2CH . CH_2 . CH(OH) . CH_2 . CO_2H$, melts at 64° (A. **283**, 143).

β-Methyl-propyl-ethylene Lactic Acid, $(CH_3)(C_3H_7)C(OH)CH_2CO_2H$, is produced in the oxidation of *methyl allyl propyl carbinol* (J. pr. Ch. [2] **23**, 267).

β-Diethyl-ethylene Lactic Acid, $(C_2H_5)_2C(OH)CH_2CO_2H$, results from the oxidation of diethyl-allyl carbinol (J. pr. Ch. [2] **23**, 201) (p. 132). *α-Methyl-ethyl-β-oxybutyric Acid*, $CH_3CH(OH) . C(CH_3)(C_2H_5)CO_2H$ (A. **188**, 266). *Tetramethyl-ethylene Lactic Acid*, $(CH_3)_2C(OH)C(CH_3)_2CO_2H$, melting at 152° (B. **28**, 2839), yields CO_2 and dimethyl isopropyl carbinol when heated. *β-Oxyisoctylic Acid*, $(CH_3)_2CH . CH_2 . CH_2CH(OH)CH_2CO_2H$, melts at 36° (A. **283**, 287).

α-Methyl propyl-β-oxybutyric Acid, $CH_3 . CH(OH) . C(CH_3)(C_3H_7)CO_2H$ (A. **226**, 288). *α-Diethyl-β-oxybutyric Acid*, $CH_3CH(OH)C(C_2H_5)_2CO_2H$ (A. **201**, 65 ; **266**, 98). *α-Dimethyl-β-isopropyl-ethylene Lactic Acid*, $(CH_3)_2CH . CH(OH) . C(CH_3)_2 .$-$CO_2H$, melts at 92° (B. **28**, 2843).

The γ- and δ-Oxyacids and their Cyclic Esters, the γ- and δ-Lactones.—The γ- and δ-oxyacids are distinguished from the α- and β-oxyacids by the fact mentioned (p. 334) that they are capable of forming simple cyclic esters, when the carboxyl group enters into reaction with the alcoholic hydroxyl group. This is a reaction that is accelerated by mineral acids in the case of the formation of the ordinary fatty acid esters. The cyclic esters of the γ- and δ-oxyacids are called γ-**Lactones** and δ-**Lactones.** In the first we have a chain of four, in the second a chain of five carbon atoms closed by oxygen. They sustain the same relation to the oxides of the γ- and δ-glycols, and to the *anhydrides of the γ- and δ-dicarbonic acids*, that the open carboxylic esters bear to the ethers of the alcohols and fatty acid anhydrides. Suppose, for example, that a hydrogen atom has been removed from each methyl group in the formulas of ethyl ether, acetic ethyl ester and acetic anhydride, and the methylene residues are then joined to each other, we then arrive at the formulas of tetramethylene oxide, γ-butyrolactone and succinic anhydride. The following scheme represents these relations:



$$\begin{array}{l}CH_3.CH_2\\CH_3.CH_2\end{array}\!>O \qquad \begin{array}{l}CH_3CO\\CH_3.CH_2\end{array}\!>O \qquad \begin{array}{l}CH_3CO\\CH_3CO\end{array}\!>O$$

Ethyl Ether — Acetic Ethyl Ester — Acetic Anhydride

$$\begin{array}{l}CH_2.CH_2\\|\\CH_2.CH_2\end{array}\!>O \qquad \begin{array}{l}\alpha CH_2CO\\|\\\beta CH_2CH_2\gamma\end{array}\!>O \qquad \begin{array}{l}CH_2CO\\|\\CH_2CO\end{array}\!>O$$

Tetramethylene Oxide — γ-Butyrolactone — Succinic Anhydride.

This lactone formation occurs more or less easily, depending upon the constitution of the γ-oxyacids. The very same causes which influence the anhydride formation with saturated and unsaturated dicarboxylic acids (see these), exert their power with the γ-oxyacids. It has been seen "that increasing magnitude or number of hydrocarbon residues in the carbon chains closed by oxygen favors the intramolecular splitting-off of water with the γ-oxyacids" (B. **24**, 1237). When the γ-oxyacids are separated from their salts by mineral acids they break down, especially on warming, almost immediately into water and lactones. It is only when the latter are boiled with alkaline carbonates that they are converted into salts of the oxyacids. This is more readily accomplished through the agency of the caustic alkalies. The γ-lactones are characterized by great stability. They are partially converted into oxy-acids by water, but this only occurs after protracted boiling, whereas those of the δ-variety gradually absorb water at the ordinary temperature and soon react acid (B. **16**, 373).

History.—The first (1873) discovered aliphatic lactone was butyrolactone, obtained by Saytzeff, who, however, regarded it as the dialdehyde of succinic acid. Erlenmeyer, Sr. (1880), expressed the opinion that lactones could only exist when they contained the group $\overline{\overset{|}{C} - C - C - CO\overset{|}{O}}$, which is present, as is well known, in the anhydrides of succinic acid (B. **13**, 305). Almost immediately afterwards J. Bredt demonstrated that isocaprolactone, from pyroterebic acid, was in fact a γ-lactone (B. **13**, 748). Fittig, as the result of a series of excellent investigations, established the genetic relations of the lactones to the oxyacids and unsaturated acids, and taught how this class of bodies could be produced by new methods. E. Fischer has shown that polyoxylactones play an especially important rôle in the synthesis of the various varieties of sugar.

The following methods answer for the formation of the *γ-oxycarboxylic acids* and their cyclic esters—the *γ-lactones:*

(1) By the reduction of the *γ-ketone carboxylic acids* with sodium amalgam:

$$\underset{\text{Lævulinic Acid}}{CH_3.CO.CH_2.CH_2.COOH} + 2H = \underset{\gamma\text{-Oxyvaleric Acid.}}{CH_3.CH(OH).CH_2.CH_2.CO_2H}$$

(2) From the *γ-halogen fatty acids:* (*a*) by distillation, when the lactones are immediately produced:

$$ClCH_2.CH_2.CH_2CO_2H \longrightarrow \overline{\overset{|}{C}H_2CH_2CH_2CO\overset{|}{O}} + HCl;$$

(*b*) by boiling them with water, or with caustic alkalies, or alkaline carbonates. In the latter case γ-lactones are even produced in the cold.

(3) From *unsaturated acids* in which the double union occurs in the $\beta\gamma$- or $\gamma\delta$-position, and from the $\Delta\beta\gamma$- or $\Delta\gamma\delta$-unsaturated acids:

(*a*) by distillation;

(*b*) by digesting them with hydrobromic acid, when an addition and separation of hydrogen bromide occur;

(*c*) by digesting them with dilute sulphuric acid (B. **16**, 373; **18**, R. 229; **29**, 1857):

$$\overset{\delta}{C}H_2 = \overset{\gamma}{C}H\overset{\beta}{C}H_2\overset{\alpha}{C}H_2CO_2H \longrightarrow CH_3\,.\,\overline{CH\,.\,CH_2\,.\,CH_2COO}$$

Allyl Acetic Acid γ-Valerolactone.

(4) By the distillation of *γ-lactone carboxylic acids* (splitting-off of CO_2 and the formation of γ-lactones), whereby the isomeric unsaturated acids are also produced (pp. 278, 284):

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!\overline{C\,.\,CH(COOH)\,.\,CH_2COO} \longrightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!>\!\overline{C\,.\,CH_2\,.\,CH_2\,.\,COO} + CO_2.$$

Terebic Acid Isocaprolactone.

The following reactions have been applied in special instances:

(5) The reduction of the chlorides and anhydrides of dibasic acids—*e.g.*, the production of γ-butyrolactone from succinyl chloride and from succinic anhydride (B. **29**, 1192).

(6) The decomposition of the reaction-products resulting from the action of halohydrins upon—

(*a*) Sodium acetoacetic ester,

(*b*) Sodium malonic ester.

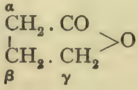
Nucleus-synthetic Methods of Formation:

(7) The action of zinc alkyls upon the chlorides of dibasic acids.

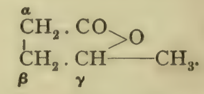
(8) CNK upon γ-halohydrins, and subsequent saponification of the resulting nitriles.

The less known *δ-oxyacids* have been prepared by the distillation of δ-chlorcarboxylic acids, or by the reduction of δ-ketone carboxylic acids.

Nomenclature.—γ-Lactones may be viewed as α-, β-, and γ-alkyl substitution products of butyrolactone, and may be named accordingly; thus, γ-methyl butyrolactone for valerolactone:



$$\begin{matrix}\overset{\alpha}{C}H_2\,.\,CO\\ \underset{\beta}{C}H_2\,.\,\underset{\gamma}{C}H_2\end{matrix}\!>\!O$$



$$\begin{matrix}\overset{\alpha}{C}H_2\,.\,CO\\ \underset{\beta}{C}H_2\,.\,\underset{\gamma}{C}H\end{matrix}\!>\!O \text{——}CH_3.$$

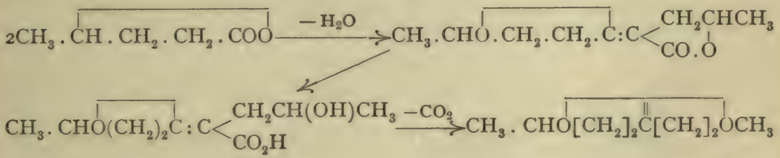
The "Geneva names" terminate in "olid"; thus, *butyrolactone* = [*Butanolid*]; *valerolactone* = [1.4-*pentanolid*].

Properties of the γ- and δ-Lactones. They are usually liquid bodies, easily soluble in water, alcohol, and ether. They show neutral reaction, possess a faintly aromatic odor, and can be distilled without decomposition. The alkaline carbonates precipitate them from their aqueous solution in the form of oils.

Deportment.—(1) They are partially converted into the corresponding oxyacids when boiled with water. A state of equilibrium arises here, which is much influenced by the number of alcohol radicals contained in the γ-lactones. (2) The lactones are changed with difficulty by the alkaline carbonates into salts of the corresponding oxyacids (B. **25**, R. 845), whereas the caustic alkalies and baryta water effect this more readily. (3) Many γ-lactones combine with the haloid acids, forming the corresponding γ-halogen fatty acids; others do not do this. In the latter the lactone union is easily severed on allowing hydrochloric or hydrobromic acid to act upon the lactones in the presence of alcohol. Then the *alkyl ethers* of the corresponding γ-chlor- and γ-brom-fatty acids are formed (B. **16**, 513).

(4) The γ-lactones unite with ammonia, but there is no separation of water (p. 348).

(5) The lactones condense under the influence of metallic sodium and sodium alcoholate. When treated with acids, an exit of water occurs, and bodies are produced which consist of the combined residues of two molecules of lactone. When these condensation products are boiled with bases, oxycarboxylic acids result, which by loss of carbon dioxide pass into *oxetones* (see these), derivatives of dioxyketones:



$$2CH_3.\overline{CH.CH_2.CH_2.COO} \xrightarrow{-H_2O} CH_3.\overline{CHO.CH_2.CH_2.C}:C<^{CH_2CHCH_3}_{CO.O}$$

$$CH_3.\overline{CHO(CH_2)_2C}:C<^{CH_2CH(OH)CH_3}_{CO_2H} \xrightarrow{-CO_2} CH_3.\overline{CHO[CH_2]_2C[CH_2]_2OCH_3}$$

γ-Lactones.

Butyrolactone [Butanolid], $\overline{\underset{\gamma}{CH_2}.\underset{\beta}{CH_2}.\underset{\alpha}{CH_2}.COO}$, boiling at 206°, has been obtained (1) by letting sodium amalgam and glacial acetic acid act on succinyl chloride (A. **171**, 261); (2) from butyrolactone carboxylic acid (see this), by the splitting-off of CO_2 (B. **16**, 2592); (3) by the distillation of γ chlorbutyric acid (B. **19**, R. 13); (4) from oxethyl acetoacetic ester, the reaction product of ethylene chlorhydrin and acetoacetic ester by decomposing it with baryta (B. **18**, R. 26); (5) by treating γ-phenoxybutyric acid with hydrobromic acid (B. **29**, R. 286).

γ-Valerolactone [1.4-Pentanolid], $\underset{\delta}{CH_3}.\overline{\underset{\gamma}{CH}.\underset{\beta}{CH_2}.\underset{\alpha}{CH_2}.COO}$, boiling at 206°, occurs in crude wood vinegar, and may be prepared (1) by the reduction of lævulinic acid, $CH_3CO.CH_2.CH_2.CO_2H$ (A. **208**, 104); (2) by boiling allyl acetic acid with dilute sulphuric acid; (3) when γ-bromvaleric acid is boiled with water; (4) on heating γ-oxypropyl malonic lactone to 220° C. (A. **216**, 56); (5) and in small quantities when methyl-paraconic acid, $CH_3.\overline{CH.CH(CO_2H).CH_2.COO}$, is distilled (A. **255**, 25). Dilute nitric acid oxidizes γ-valerolactone to ethylene succinic acid, while HI converts it into n-valeric acid. α-**Methyl butyrolactone**, $\overline{CH_2.CH_2CH(CH_3).COO}$, boils at 201° (B. **28**, 10; **29**, 1194).

Caprolactones. γ-n-*Caprolactone*, γ-ethyl butyrolactone, [1.4-Hexanolid], $CH_3 . CH_2 . CH . CH_2 . CH_2 . COO$, boiling at 220°, is formed by the general methods 2, 3, and 4. It also appears in the reduction of gluconic acid, metasaccharic acid and galactonic acid by hydriodic acid (B. **17**, 1300; **18**, 642, 1555).

β-Methyl valerolactone, βγ-Dimethyl butyrolactone, $CH_3 . CH . CHCH_3)$-CH_2COO, boiling at 209°, is obtained from β-acetobutyric acid. α-**Ethyl-butyrolactone,** $CH_2 . CH_2 . CH(C_2H_5)COO$, boiling at 215°, is formed from ethoxy-ethyl acetoacetic ester. *αγ-Dimethyl-butyrolactone*, $CH_3 . CH . CH_2 . CH(CH_3)COO$, boiling at 206°, is prepared from β aceto-isobutyric acid.

Isocaprolactone, $(CH_3)_2C . CH_2 . CH_2 . COO$, melting at 7° and boiling at 207°, is produced together with pyroterebic acid in the distillation of terebic acid. (See general method 4, p. 343.) Pyroterebic acid itself passes on long boiling into isocaprolactone. It can also be obtained from isobutyric aldehyde, malonic acid, and acetic anhydride (B. **29**, R. 667).

Heptolactones. γ-n-*Heptolactone*, γ-n-Propylbutyrolactone, $CH_3 . CH_2 . CH_2$-$CHCH_2CH_2COO$, boiling at 235°, is obtained from γ-bromœnanthic acid, from n-propylparaconic acid, and from dextrose-carboxylic acid, as well as from galactose carboxylic acid on treatment with hydriodic acid (B. **21**, 918). *γ-Isopropylbutyrolactone*, $(CH_3)_2CH . CHCH_2CH_2COO$, boiling at 224°, is formed, along with isoheptylic acid, from isopropylparaconic acid. *α-Ethyl Valerolactone*, CH_3.-$CH . CH_2 . CH(C_2H_5)COO$, boiling at 219°, is obtained from α-ethyl-β-acetopropionic acid and from allyl ethyl acetic acid by general method 3 (B. **29**, 1857). *α-Dimethyl Valerolactone*, $CH_3 . CH . CH_2 . C(CH_3)_2COO$, melting at 52° and boiling at 86° (15 mm.), may be obtained from α-dimethyl-lævulinic acid or mesitonic acid (see this).

Octolactones. *γ-Isobutylbutyrolactone*, $(CH_3)_2CHCH_2CHCH_2CH_2COO$, is obtained from isobutylparaconic acid. *α-Propylvalerolactone* boils at 233°. *α-Isopropylvalerolactone* boils at 224° (B. **29**, 1857, 2001). *α-Ethyl-β-methylvalerolactone*, $CH_3CH . CH(CH_3)CH(C_2H_5)COO$, boiling at 226–227°, is obtained from α-ethyl-β-methylacetopropionic acid. *γ-Diethylbutyrolactone*, $C(C_2H_5)_2CH_2CH_2COO$, boiling from 228–233°, has been prepared from succinyl chloride and zinc ethide. *α-Methyl-γ-isobutylbutyrolactone*, $(CH_3)_2CH . CH_2 . CH . CH_2 . CH(CH_3) . COO$, has been obtained from α-methylisobutylparaconic acid. γ-**Hexylbutyrolactone,** CH_3-$(CH_2)_5 . CHCH_2CH_2COO$, boils at 281° C.

δ-Lactones.

Certain aliphatic δ-lactones are known. They have been prepared by the distillation of the corresponding δ-chlor-acids, or by the reduction of δ-ketone carboxylic acids (see these): *δ-Valerolactone*, $CH_2 . CH_2 . CH_2 . CH_2 . COO$, boils at 230° (B. **26**, 2574). *δ-Caprolactone*, $CH_3 . CH . CH_2 . CH_2 . CH_2 . COO$, melts at 13° and boils at 275°. *γ-Ethyl-capro-δ-lactone*, $CH_3 . CHCH(C_2H_5)CH_2 . CH_2COO$, boils at 254–255° (A. **216**, 127; **268**, 117).

Sulphur Derivatives of the Oxy-acids: Glycollic and Lactic Acids.

Only the mercaptan carboxylic acids and their transposition products will be considered here. These are acids which at the same time possess the nature of a mercaptan. They are obtained as oils, with a disagreeable odor. They are miscible with water, alcohol and ether.

(1) *a-Mercaptan Carboxylic Acids.*

Thioglycollic Acid, $CH_2<\begin{smallmatrix}SH\\CO_2H\end{smallmatrix}$ [Ethanthiol Acid], is obtained from monochloracetic acid and potassium sulphydrate, and from thiohydantoïn, when heated with alkalies (A. **207,** 124). On adding ferric chloride to its solution, we obtain an indigo-blue coloration. It is a dibasic acid. The *barium salt,* $CH_2<\begin{smallmatrix}S\\CO_2\end{smallmatrix}>Ba + 3H_2O$, dissolves with difficulty in water.

a-Thiolactic Acid, $CH_3.CH(SH)CO_2H$, is obtained from pyroracemic acid and hydrogen sulphide.

(2) *a-Alkyl Sulphide Carboxylic Acids* are obtained from the interaction of *a*-halogen fatty acids and sodium mercaptides.

(3) *a-Mercaptal Carboxylic Acids* result from the action of *a*-thio-acids and aldehydes. *Ethidene-dithioglycollic Acid,* $CH_3.CH:(SCH_2.COOH)_2$, melts at 107°.

(4) *a-Mercaptol Carboxylic Acids* result from *a*-thio-acids and ketones in the presence of zinc chloride or HCl.

Dimethylene-dithioglycollic Acid, $(CH_3)_2C:(SCH_2COOH)_2$, melts at 126°.

(5) *a-Sulphide Dicarboxylic Acids* are produced when K_2S acts upon *a*-halogen fatty acids.

Thiodiglycollic Acid, $S<\begin{smallmatrix}CH_2.CO_2H\\CH_2.CO_2H\end{smallmatrix}$, melts at 129°. In composition it corresponds to diglycollic acid (p. 339), and under like conditions forms a cyclic anhydride, which is both a sulphide and a carboxylic anhydride. *Thiodiglycollic Anhydride,* $S<\begin{smallmatrix}CH_2CO\\CH_2CO\end{smallmatrix}>O$, melts at 102°, and boils at 158° (10 mm.) (B. **27,** 3059). *a-Thiodilactyl Acid,* $S[CH(CH_3).CO_2H]_2$, melts at 125°. *γ-Thiodibutyric Acid* melts at 99° (B. **25,** 3040). Unsymmetrical *Sulphide dicarboxylic acids* are obtained from the disodium salts of the mercaptan carboxylic acids and sodium halogen fatty acids in aqueous solution (B. **29,** 1139).

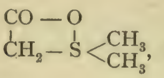
(6) *a-Disulphide Dicarboxylic Acids* are readily produced in the oxidation of the *a*-mercaptan carboxylic acids in the air, or with ferric chloride or iodine. *Dithiodiglycollic Acid,* $(SCH_2CO_2H)_2$, melts at 100°. *a-Dithiodilactic Acid,* $[SCH(CH_3).CO_2H]_2$, melts at 141°.

Cysteïn is probably an *amido-thiolactic acid,* $CH_3.C\left(\begin{smallmatrix}SH\\NH_2\end{smallmatrix}\right).CO_2H$. It is obtained from cystin by reduction with tin and hydrochloric acid. A crystalline powder, very soluble in water, and yielding an indigo-blue color with ferric chloride. In the air it rapidly oxidizes to cystin (B. **18,** 258, and **19,** 125).

Cystin, $C_6H_{12}N_2O_4S_2$, probably dithio-diamido-dilactic acid, $S_2<\begin{smallmatrix}C(CH_3)(NH_2).CO_2H\\C(CH_3)(NH_2).CO_2H\end{smallmatrix}$, occurs in some calculi and urinary sediments. It forms colorless leaflets. It is insoluble in water and alcohol, but dissolves in acids and alkalies.

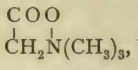
(7) *Sulphin-oxide Carboxylic Acids.*—The free bodies—*e. g.*, $\begin{array}{l}COOH\\|\\CH_2S(CH_3)_2OH\end{array}$, are unstable. They split off water and yield *cyclic sulphinates,* which are constituted similarly to the cyclic ammonium compounds, and are called *thetines.* This name,

from the contraction of *thio* and *betaïne*, is intended to express the analogy between their derivatives and betaïne (B. **7**, 695; **25**, 2450; **26**, R. 409):



$$\begin{matrix} CO - O \\ | \quad\;\; | \\ CH_2 - S<{CH_3 \atop CH_3} \end{matrix}$$

Dimethyl Thetine;



$$\begin{matrix} COO \\ | \quad | \\ CH_2N(CH_3)_3 \end{matrix}$$

betaïne, p. 310.

The thetines are feeble bases. Their hydrobromides are produced when methyl sulphide, ethyl sulphide, and sodium thio-diglycollate are brought into action with *a*-halogen fatty acids—*e. g.*, chloracetic acid and *a*-brompropionic acid.

Dimethyl Thetine, $\overline{(CH_3)_2S . CH_2 . CO . O}$, is deliquescent.

Dimethyl Thetine Dicarboxylic Acid, $(HO . CO . CH_2)_2\overline{S . CH_2 . COO}$, melts at 157–158°.

Selenetines, see B. **27**, R. 801.

(8) *Sulphone Carboxylic Acids* are produced by the action of alkyl sulphinates upon esters of halogen fatty acids. They recall the ketone carboxylic acids (see these). *Ethyl Sulphone Acetic Acid*, $C_2H_5 . SO_2 . CH_2 . CO_2H$. *Ethyl Sulphone Propionis Acid*, $C_2H_5 . SO_2 . CH_2 . CH_2 . CO_2H$ (B. **21**, 89, 992). By oxidizing the sulphide, corresponding to the sulphones with $KMnO_4$ we obtain: *Sulphone Diacetic Acid*, $O_2S(CH_2CO_2H)_2$, melting at 182°. *a-Sulphone Dipropionic Acid*, $O_2S[CH(CH_3) . CO_2H]_2$, melts at 155° (B. **18**, 3241). Sulphone diacetic acid resembles aceto-acetic ester in many respects. For mixed sulphone-di-fatty acids see B. **29**, 1141.

(9) *a-Sulpho-carboxylic Acids.* The sulpho-acids of the fatty acids are produced by methods similar to those employed with the alkyl sulphonic acids:

(1) By the action of sulphur trioxide upon the fatty acids, or by acting with fuming sulphuric acid on the nitriles, or amides of the acids.

(2) By heating concentrated aqueous solutions of the salts of the monosubstituted fatty acids with alkaline sulphites.

(3) By the addition of alkaline sulphites to unsaturated acids (B. **18**, 483).

(4) By oxidizing the thio-acids corresponding to the oxy-acids with nitric acid.

(5) Upon oxidizing glycol sulphonic acids, *e. g.*, isethionic acid, with nitric acid.

These sulpho-acids are dibasic acids. They correspond to the dicarboxylic acids, like malonic acid. The sulpho-group in them is not so intimately combined as in the sulphonic acids of the alcohol radicals. Boiling alkalies convert them into oxy-acids.

Sulpho-acetic Acid, $CH_2<{SO_2 . OH\,1\frac{1}{2}H_2O \atop CO_2H}$, fuses at 75°. Pentachloride of phosphorus converts it into a chloride, $CH_2<{SO_2Cl \atop CO . Cl}$, boiling at 130–135° (150 mm.). By reduction of the latter thio-glycollic acid is produced.

Its *diethyl ester* is not volatile without decomposition. The hydrogen atoms of the CH_2-group in this ester (as in acetoacetic and malonic esters) can be replaced by alkyls (B. **21**, 1550).

NITROGEN DERIVATIVES OF THE OXY-ACIDS.

The following classes of nitrogen compounds are derived from the *a-alcohol acids:* 1. Oxy-amides. 2. Oxy-hydrazides. 3. Oxy-azides. 4. Oxy-nitriles. 5. Hydroxylamine fatty acids. 6. Amidoxyl fatty acids. 7. Nitro-fatty acids. 8. Amido-fatty acids. 9. Nitramine fatty acids. 10. Isonitramine fatty acids. 11*a*. Hydrazino-fatty acids. 11*b*. Hydrazo-fatty acids. 12. Azo-fatty acids.

Glycocoll or amido-acetic acid, and certain derivatives, like the leucines, are among the more important *a*-amido-fatty acids from a physiological standpoint.

1. **Oxyamides.**—The *a*-oxyamides are produced (1) by treating (*a*) alkyl esters and (*b*) cyclic double esters of the lactides with ammonia. (2) From the *a*-oxynitriles by the absorption of water in the presence of a mineral acid, particularly sulphuric acid. They behave like the fatty acid amides.

Glycollamide, $CH_2<\begin{smallmatrix}OH\\CO\,.\,NH_2\end{smallmatrix}$, is obtained from polyglycollide, or from acid ammonium tartronate when heated to 150°. It melts at 120°, and possesses a sweet taste.

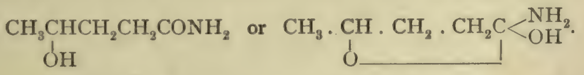
Lactamide, $CH_3\,.\,CH<\begin{smallmatrix}OH\\CO\,.\,NH_2\end{smallmatrix}$, melts at 74°.

a-Oxycaprylamide, $CH_3(CH_2)_5CH(OH)CONH_2$, melts at 150° (A. **177**, 108). Diglycollic acid yields two amides and a cyclic imide:

Diglycollamic Acid, $NH_2CO\,.\,CH_2\,.\,O\,.\,CH_2\,.\,CO_2H$, melts at 135°.

Diglycollamide, $O(CH_2CONH_2)_2$, breaks down when heated into ammonia and *diglycollimide,* $O<\begin{smallmatrix}CH_2\,.\,CO\\CH_2\,.\,CO\end{smallmatrix}>NH$, melting at 142°. It deports itself like the imides of the dicarboxylic acids, *e. g.*, succinimide (see this) and n-glutarimide.

The readily decomposable additive products, arising from ammonia and the γ-lactones (A. **256**, 147), are viewed as γ-oxyacid amides. Yet they are said to have a constitution similar to aldehyde-ammonia (A. **259**, 143). The additive product from ammonia and γ-valerolactone may have one of the following formulas:



$$\underset{\displaystyle OH}{CH_3\overset{}{CH}}CH_2CH_2CONH_2 \quad \text{or} \quad CH_3\,.\,\underset{\displaystyle O\text{———}}{CH}\,.\,CH_2\,.\,CH_2C<\begin{smallmatrix}NH_2\\OH\end{smallmatrix}.$$

2. **Hydrazides of the Oxyacids:** *Glycol Hydrazide,* $HO\,.\,CH_2\,.\,CO\,.\,NH\,.\,NH_2$, melting at 93°, has been prepared from benzoyl or oxalyl glycollic ester and hydrazine hydrate (J. pr. Ch. [2] **51**, 365).

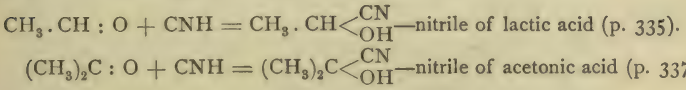
3. **Azides of the Oxyacids:** *Glycol Azide,* $HO\,.\,CH_2\,.\,CON_3$, is formed when sodium nitrite acts upon the hydrochloride of glycol hydrazide. It crystallizes from ether (J. pr. Ch. [2] **52**, 225).

4. Nitriles of the Oxy-acids.

The nitriles of the *a*-oxy-acids are the additive products obtained from hydrocyanic acid and the aldehydes, and ketones.

The *aldehydes* yield *nitriles of secondary oxy-acids.* Formaldehyde is an exception in this respect, for it affords the nitrile of a primary oxy-acid,—glycollic acid.

The *ketones* yield *nitriles of tertiary oxy-acids.*



$$CH_3\,.\,CH:O + CNH = CH_3\,.\,CH<\begin{smallmatrix}CN\\OH\end{smallmatrix}\text{—nitrile of lactic acid (p. 335).}$$

$$(CH_3)_2C:O + CNH = (CH_3)_2C<\begin{smallmatrix}CN\\OH\end{smallmatrix}\text{—nitrile of acetonic acid (p. 337).}$$

These nitriles of the *a*-oxy-acids have been called the cyanhydrins of the dihydric alcohols or glycols, which can not exist. Their anhydrides are probably the aldehydes and ketones.

The anhydrous bodies boil in part without decomposition; many of them break down upon the evaporation of their aqueous solution, and alkalies resolve them into their components. The nitriles of the α-oxy-acids, on the other hand, under the influence of mineral acids, *e. g.*, hydrochloric acid and sulphuric acid, first take up one molecule of water and change to α-oxy acid amides (see above), then a second molecule of water, and form the ammonium salts of the α-oxy-acids, which are immediately decomposed by mineral acids (p. 264).

Aldehyde Cyanhydrins: *Glycollic Nitrile* [Ethanol Nitrile], $HOCH_2CN$, boils at 183° with slight decomposition. It boils at 119° (24 mm.) (B. **23**, R. 385). *Ethidene Lactic Nitrile*, aldehyde cyanhydrin, $CH_3CH(OH)CN$, boils with decomposition at 182°. *Ethyl Ether*, $CH_3CH(OC_2H_5)CN$, from chlorcyanogen and ethyl ether, boils at 88° (B. **28**, R. 15). *Acetyl Ether*, $CH_3CH(OCOCH_3)CN$, boils at 169° (B. **28**, R. 109). *β-Ethoxybutyronitrile*, $CH_3CH(OC_2H_5).CH_2CN$, from cyanallyl and ethyl alcohol, boils at 173° (B. **29**, 1425). *α-Oxyisovaleric Nitrile*, $(CH_3)_2CH.CH(OH)CN$, breaks down at 135°. *α-Oxycaprylic Nitrile*, œnanthol hydrocyanide, $CH_3(CH_2)_5CH(OH)CN$.

Halogen Substitution Products of the Aldehyde Cyanhydrins (A. **179**, 73): *Chloral Cyanhydrin*, $CCl_3CH(OH)CN$, melting at 61°, boils with decomposition at 215–230°. *Tribromlactic Acid Nitrile*, $CBr_3CH(OH)CN$. *Trichlorvalerolactic Acid Nitrile*, $CH_3.CCl_2.CHCl.CH(OH)CN$, melts at 102–103°. **Ketocyanhydrins**: *α-Oxyisobutyric Acid Nitrile*, $(CH_3)_2C(OH)CN$, boils at 120°. *Methyl Ethyl Glycollic Acid Nitrile*, $(C_2H_5)(CH_3).C(OH)CN$ (A. **204**, 18). *Diethyloxalic Acid Nitrile*, diethyl glycollic nitrile, $(C_2H_5)_2C(OH)CN$ (B. **14**, 1974).

Nitriles of the oxy-acids have been prepared from the halogen glycolhydrins (p. 300) by the action of potassium cyanide. *Ethylene Cyanhydrin*, β-Lactic Acid Nitrile, $HO.CH_2.CH_2CN$, boiling at 220°, is also obtained from ethylene oxide and prussic acid. In many cases the nitriles of the oxy-acids have not been worked out, but have either been immediately changed to oxy-acids, or have been drawn into the circle of other reactions.

5. **Hydroxylamine Acetic Acid**, $NH_2O.CH_2.CO_2H$, has been obtained as its hydrochloride, melting at 148°, together with benzoic ester, from ethyl benzhydroxime-acetic acid, $C_6H_5(O.C_2H_5):NOCH_2CO_2H$. The free acid is a gummy mass. For homologues see B. **29**, 2654.

6. **Amidoxyl Fatty Acids** are isomeric with the hydroxylamine fatty acids. Their nitriles result from the addition of hydrocyanic acid to aldoximes and ketoximes (B. **29**, 65). *Amidoxyl Acetic Acid*, $HO.NH.CH_2.CO_2H$, melting at 132°, is formed by the action of concentrated hydrochloric acid upon isobenzaldoxime acetic acid, and dilute mineral acids upon (B. **29**, 667) isonitramine acetic acid. *α-Amidoxyl-butyro-nitrile*, $CH_3.CH_2.CH(NHOH)CN$, melting at 86°, is obtained from propylaldoxime and prussic acid. Concentrated sulphuric acid converts it into α-isonitroso- or α-oximido-butyric acid, and cold hydrochloric acid changes it to α-amidoxylbutyric acid, which decomposes at 166° (B. **26**, 1548).

7. **Nitrofatty Acids. α-Nitrofatty Acids.**—*Nitroacetic Acid* is only known in the form of its ethyl ester. When potassium nitrite acts upon potassium chloracetate the potassium nitroacetate produced at first breaks down into nitromethane (p. 155) and potassium monocarbonate:

$$CH_2Cl\,COOK + NO_2K = CH_2NO_2.COOK + KCl$$
$$CH_2NO_2\,COOK + H_2O = CH_3NO_2 + KHCO_3.$$

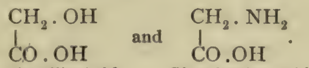
Nitroacetic Ethyl Ester, $NO_2CH_2.CO_2C_2H_5$, boils with scarcely any decomposition, at 151°. It is produced when bromacetic ester and silver nitrite interact. Hydrochloric acid and tin convert it into amidoacetic acid.

β-Nitrofatty Acids: *β-Nitropropionic Acid*, $NO_2CH_2.CH_2CO_2H$, melting at 66°, is formed from β-iodopropionic acid and silver nitrite. The *ethyl ester* boils from 161–165°.

β-Nitro-isovaleric Acid, $(CH_3)_2C(NO_2)CH_2CO_2H$, is formed together with *dinitropropane*, $(CH_3)_2C(NO_2)_2$, when nitric acid acts upon isovaleric acid (B. 15, 2324).

8. Amido- or Amino-fatty Acids.

In the amido-acids the alcoholic hydroxyl of the dihydric acids is replaced by the amido-group NH_2:



$$\begin{array}{l} CH_2.OH \\ | \\ CO.OH \end{array} \quad \text{and} \quad \begin{array}{l} CH_2.NH_2 \\ | \\ CO.OH \end{array}.$$

Glycollic Acid Glycolamino-acid.

It is simpler to view them as amido-derivatives of the monobasic fatty acids, produced by the replacement of one hydrogen atom in the latter by the amido-group:

$$\begin{array}{l} CH_3 \\ | \\ CO.OH \end{array} \qquad \begin{array}{l} CH_2.NH_2 \\ | \\ CO.OH \end{array}.$$

Acetic Acid Amidoacetic Acid.

Hence they are usually called *amido-fatty acids*. The firm union of the amido-group in them is a characteristic difference between these compounds and their isomeric acid amides. Boiling alkalies do not eliminate it (similar to the amines). Several of these amido-acids occur already formed in plant and animal organisms. Great physiological importance attaches to them here. They can be obtained from albuminoid substances by heating the latter with hydrochloric acid or baryta water. They have received the name *alanines* or *glycocolls* from their most important representatives.

The general methods in use for preparing the amido-acids are:

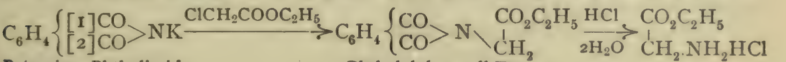
(1) The transposition of the monohalogen fatty acids when heated with ammonia (similar to the formation of the amines from the alkylogens, p. 161):

Thus chloracetic acid yields:

$$N\left\{\begin{array}{l} CH_2.COOH \\ H \\ H \end{array}\right. \qquad N\left\{\begin{array}{l} CH_2.COOH \\ CH_2.COOH \\ H \end{array}\right. \qquad N\left\{\begin{array}{l} CH_2.COOH \\ CH_2.COOH \\ CH_2.COOH \end{array}\right.$$

Amido-acetic Acid Diglycolamidic Acid Triglycolamidic Acid.

(2) In the action of the halogen fatty acids upon ammonia, phthalimide may be employed to promote the reaction, in that the halogen fatty-acid esters are allowed to react with potassium phthalimide, after which the amido-acid is split off by hydrochloric acid at 200° C.:



$$C_6H_4\left\{\begin{array}{l}[1]CO\\ [2]CO\end{array}\right\rangle NK \xrightarrow{ClCH_2COOC_2H_5} C_6H_4\left\{\begin{array}{l}CO\\ CO\end{array}\right\rangle N\diagdown \begin{array}{l}CO_2C_2H_5\\ |\\ CH_2\end{array} \xrightarrow[2H_2O]{HCl} \begin{array}{l}CO_2C_2H_5\\ |\\ CH_2.NH_2HCl\end{array}$$

Potassium Phthalimide Phthalylglycocoll Ester.

(3) The reduction of nitro- and isonitroso-acids (p. 350) with nascent hydrogen (Zn and HCl):

$$CH_2NO_2.CO.O.C_2H_5 \xrightarrow{4H} CH_2NH_2.COOH$$

Nitro-acetic Ester Amido-acetic Acid

$$CH_3.C:(NOH).COOH \xrightarrow{4H} CH_3.CH(NH_2)COOH$$

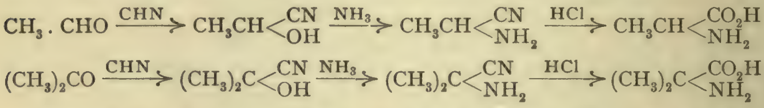
α-Oximidopyroracemic Acid Alanine, α-Amidopropionic Acid.

(4) Transposition of the cyan-fatty acids (see these) with nascent H (Zn and HCl, or by heating with HI), in the same manner that the amines are produced from the alkyl cyanides (p. 266):

$$\underset{\text{Cyanformic Acid}}{\mathrm{CN.CO.OH}} + 2\mathrm{H_2} = \underset{\text{Amido-acetic Acid.}}{\mathrm{CH_2(NH_2).CO_2H}}$$

This reaction connects the amido-fatty acids with the fatty acids containing an atom less of carbon, and also with the dicarboxylic acids of like carbon content, whose *half nitriles* are the cyan-fatty acids.

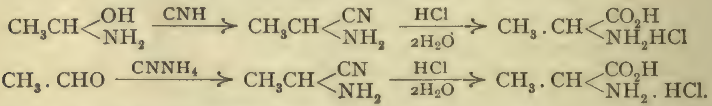
(5) The nitriles of the *α*-amido-acids are prepared by allowing a calculated quantity of ammonia, in alcoholic solution, to act upon the hydrocyanic acid additive products of the aldehydes and ketones, and then setting free the hydrochlorides of the *α*-amido-acids from these by means of hydrochloric acid (B. **13**, 381; **14**, 1965):



$$\mathrm{CH_3.CHO} \xrightarrow{\mathrm{CHN}} \mathrm{CH_3CH}{<}\begin{smallmatrix}\mathrm{CN}\\ \mathrm{OH}\end{smallmatrix} \xrightarrow{\mathrm{NH_3}} \mathrm{CH_3CH}{<}\begin{smallmatrix}\mathrm{CN}\\ \mathrm{NH_2}\end{smallmatrix} \xrightarrow{\mathrm{HCl}} \mathrm{CH_3CH}{<}\begin{smallmatrix}\mathrm{CO_2H}\\ \mathrm{NH_2}\end{smallmatrix}$$

$$\mathrm{(CH_3)_2CO} \xrightarrow{\mathrm{CHN}} \mathrm{(CH_3)_2C}{<}\begin{smallmatrix}\mathrm{CN}\\ \mathrm{OH}\end{smallmatrix} \xrightarrow{\mathrm{NH_3}} \mathrm{(CH_3)_2C}{<}\begin{smallmatrix}\mathrm{CN}\\ \mathrm{NH_2}\end{smallmatrix} \xrightarrow{\mathrm{HCl}} \mathrm{(CH_3)_2C}{<}\begin{smallmatrix}\mathrm{CO_2H}\\ \mathrm{NH_2}\end{smallmatrix}.$$

(6) Nitriles of *α*-amido-acids can also be synthetically obtained (*a*) from the aldehyde ammonias by means of hydrocyanic acid; (*b*) from aldehydes by means of ammonium cyanide (B. **14**, 2686):



$$\mathrm{CH_3CH}{<}\begin{smallmatrix}\mathrm{OH}\\ \mathrm{NH_2}\end{smallmatrix} \xrightarrow{\mathrm{CNH}} \mathrm{CH_3CH}{<}\begin{smallmatrix}\mathrm{CN}\\ \mathrm{NH_2}\end{smallmatrix} \xrightarrow[\mathrm{2H_2O}]{\mathrm{HCl}} \mathrm{CH_3.CH}{<}\begin{smallmatrix}\mathrm{CO_2H}\\ \mathrm{NH_2HCl}\end{smallmatrix}$$

$$\mathrm{CH_3.CHO} \xrightarrow{\mathrm{CNNH_4}} \mathrm{CH_3CH}{<}\begin{smallmatrix}\mathrm{CN}\\ \mathrm{NH_2}\end{smallmatrix} \xrightarrow[\mathrm{2H_2O}]{\mathrm{HCl}} \mathrm{CH_3.CH}{<}\begin{smallmatrix}\mathrm{CO_2H}\\ \mathrm{NH_2}\end{smallmatrix}\mathrm{.HCl.}$$

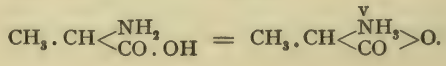
Prussic acid attaches itself similarly to the oximes (B. **25**, 2070), to the hydrazones, and to the Schiff bases, with the production of nitriles (B. **25**, 2020).

The 5th and 6th methods are only suitable for the production of *α*-amido-fatty acids, while the remaining methods serve also for the preparation of *β*-, *γ*-, and *δ*-amido-fatty acids, which are also produced:

(7) By the addition of ammonia to unsaturated acids, as well as (8*a*) by the oxidation of amido-ketones, *e. g.*, diacetonamine (p. 219), and (8*b*) by the breaking down of the cyclic imides of glycols upon oxidation, see *piperidine*.

Properties.—The amido-acids are crystalline bodies with usually a sweet taste, and are readily soluble in water. As a general thing, they are insoluble in alcohol and ether.

Constitution.—As the amido-acids contain both a carboxyl and an amido-group, they are acids and bases. Since, however, the carboxyl and amido-groups mutually neutralize each other, the amido-acids show neutral reaction, and it is very probable that both groups combine to produce a cyclic ammonium salt:

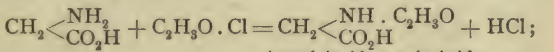


$$\mathrm{CH_3.CH}{<}\begin{smallmatrix}\mathrm{NH_2}\\ \mathrm{CO.OH}\end{smallmatrix} = \mathrm{CH_3.CH}{<}\begin{smallmatrix}\overset{\mathrm{V}}{\mathrm{N}}\mathrm{H_3}\\ \mathrm{CO}\end{smallmatrix}{>}\mathrm{O.}$$

The existence and method of producing trimethyl glycocoll or betaïne would indicate this. A separation of the two groups would again occur in the formation of the salts.

Deportment.—The amido-acids form (1) metallic salts with metallic oxides, and (2) ammonium salts with acids.

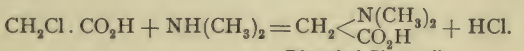
(3) The hydrogen of the carboxyl group can be replaced by alcohol radicals with formation of *esters*, which are, however, unstable. On the other hand, the hydrogen of the amido-group can be replaced by both acid and alcohol radicals. (4) The *acid derivatives* appear when acid chlorides act upon the amido-acids or their esters:



$$CH_2<\genfrac{}{}{0pt}{}{NH_2}{CO_2H} + C_2H_3O.Cl = CH_2<\genfrac{}{}{0pt}{}{NH.C_2H_3O}{CO_2H} + HCl;$$

Acetyl Amido-acetic Acid.

whereas (5) the *alcohol derivatives* are obtained by the action of the amines on substituted fatty acids:



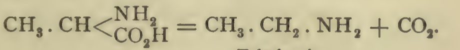
$$CH_2Cl.CO_2H + NH(CH_3)_2 = CH_2<\genfrac{}{}{0pt}{}{N(CH_3)_2}{CO_2H} + HCl.$$

Dimethyl Glycocoll.

(6) By continuing the introduction of methyl into the amido-acids it is possible to entirely split off the amido-group. Unsaturated acids result. Thus, α-amidopropionic acid yields acrylic acid, and α-amido-butyric acid yields crotonic acid (B. **21**, R. 86), while α-amido-n-valeric acid yields propylidene acetic acid (B. **26**, R. 937).

(7) When the amido-acids are heated to 200° with hydriodic acid they exchange their amido-group for hydrogen and become fatty acids (B. **24**, R. 900).

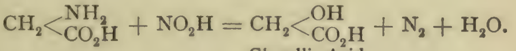
They are not affected by boiling alkalies, but (8) when fused they decompose into salts of the fatty acids and into amines or ammonia. (9) By dry distillation (with baryta especially) they yield amines and carbon dioxide:



$$CH_3.CH<\genfrac{}{}{0pt}{}{NH_2}{CO_2H} = CH_3.CH_2.NH_2 + CO_2.$$

Ethylamine.

(10) Nitrous acid converts them into oxy-acids:

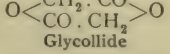


$$CH_2<\genfrac{}{}{0pt}{}{NH_2}{CO_2H} + NO_2H = CH_2<\genfrac{}{}{0pt}{}{OH}{CO_2H} + N_2 + H_2O.$$

Glycollic Acid.

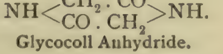
(11) When potassium nitrite is allowed to act on the hydrochlorides of the esters of the amido-acids, esters of the diazo-fatty acids (p. 365) are produced. Their formation serves as a test for even minute quantities of the amido-acids (B. **17**, 959). Ferric chloride yields a red color with all the amido-acids. Acids discharge the same.

One of the chief characteristics of the α-amido-fatty acids is that when they lose water they yield cyclic double acid amides, corresponding to the cyclic double esters of the α-oxy-acids or lactides (p. 339):



$$O<\genfrac{}{}{0pt}{}{CH_2.CO}{CO.CH_2}>O$$

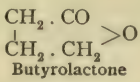
Glycollide



$$NH<\genfrac{}{}{0pt}{}{CH_2.CO}{CO.CH_2}>NH.$$

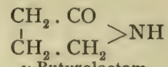
Glycocoll Anhydride.

The γ- and δ-amido-acids, however, are capable of forming cyclic, simple acid amides, the so-called γ- and δ-lactams, corresponding to the γ- and δ-lactones, the cyclic, simple esters of the γ- and δ-oxy-acids:



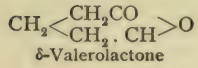
$$\begin{matrix} CH_2.CO \\ | \\ CH_2.CH_2 \end{matrix} > O$$

Butyrolactone



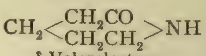
$$\begin{matrix} CH_2.CO \\ | \\ CH_2.CH_2 \end{matrix} > NH$$

γ-Butyrolactam,
Pyrrolidone



$$CH_2 < \begin{matrix} CH_2CO \\ CH_2.CH \end{matrix} > O$$

δ-Valerolactone

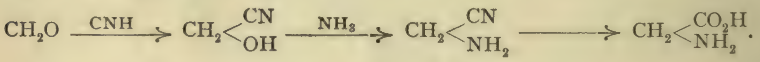


$$CH_2 < \begin{matrix} CH_2CO \\ CH_2CH_2 \end{matrix} > NH$$

δ-Valerolactam,
α-Oxopiperidine.

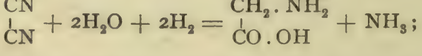
α-Amido-acids.

Glycocoll, *Glycin, Amido-acetic Acid* [*Amino-ethan Acid*], $CH_2(NH_2).CO_2H$, melting at 232–236°, is obtained synthetically (p. 352): (1) By heating monochloracetic acid with ammonia (di- and triglycolamidic acids are formed at the same time) or by warming monochloracetic acid with dry ammonium carbonate (B. **16**, 2827); (2) from phthalylglycocoll ester (B. **22**, 426); (3) by the reduction of nitro-acetic acid; (4) of cyan-formic acid; (5) by heating methylene amido-acetonitrile with alcoholic hydrochloric acid, when it changes to the hydrochloride of glycin ester (B. **29**, 762); (6) from methylene cyanhydrin, the product obtained by the union of formaldehyde and prussic acid. Ammonia converts it into glycocoll nitrile, which is altered to glycocoll by boiling baryta water (A. **278**, 229):



$$CH_2O \xrightarrow{CNH} CH_2 < \begin{matrix} CN \\ OH \end{matrix} \xrightarrow{NH_3} CH_2 < \begin{matrix} CN \\ NH_2 \end{matrix} \xrightarrow{\qquad} CH_2 < \begin{matrix} CO_2H \\ NH_2 \end{matrix}.$$

Glycocoll may be prepared by methods 2, 5, and 6, or by the decomposition of hippuric acid (see below). A rather striking formation of glycocoll is observed (7) by conducting cyanogen gas into boiling hydriodic acid:

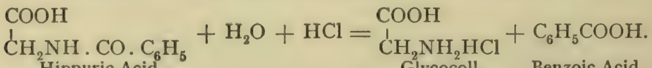


$$\begin{matrix} CN \\ | \\ CN \end{matrix} + 2H_2O + 2H_2 = \begin{matrix} CH_2.NH_2 \\ | \\ CO.OH \end{matrix} + NH_3;$$

and, finally, (8) by letting ammonium cyanide and sulphuric acid act upon glyoxal, when the latter probably at first yields formaldehyde (B. **15**, 3087).

History and Occurrence.—Braconnot (1820) first obtained glycocoll by decomposing glue with boiling sulphuric acid. It owes its name to this method of formation and to its sweet taste: γλυκύς, sweet, κόλλα, glue.

Dessaignes (1846) showed that glycocoll was formed as a decomposition product when hippuric acid was boiled with concentrated hydrochloric acid:



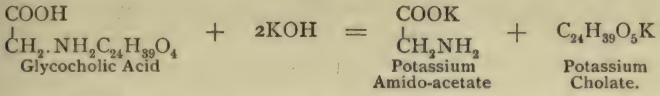
$$\begin{matrix} COOH \\ | \\ CH_2NH.CO.C_6H_5 \end{matrix} + H_2O + HCl = \begin{matrix} COOH \\ | \\ CH_2NH_2HCl \end{matrix} + C_6H_5COOH.$$

Hippuric Acid
Benzoyl Glycocoll

Glycocoll
Hydrochloride

Benzoic Acid.

Strecker (1848) observed that glycocoll appeared from an analogous decomposition of the glycocholic acid occurring in bile. Compare taurine, p. 306:



$$\underset{\text{Glycocholic Acid}}{\begin{array}{l}COOH\\ |\\ CH_2.NH_2C_{24}H_{39}O_4\end{array}} + 2KOH = \underset{\text{Potassium Amido-acetate}}{\begin{array}{l}COOK\\ |\\ CH_2NH_2\end{array}} + \underset{\text{Potassium Cholate.}}{C_{24}H_{39}O_5K}$$

Glycocoll was first (1858) prepared artificially by Perkin and Duppa, when they allowed ammonia to act upon bromacetic acid.

Properties.—Glycocoll crystallizes from water in large, rhombic prisms, which are soluble in 4 parts of cold water. It is insoluble in alcohol and ether. It possesses a sweetish taste, and melts with decomposition. Heated with baryta it breaks up into methylamine and carbon dioxide; nitrous acid converts it into glycollic acid. Ferric chloride imparts an intense red coloration to glycocoll solutions; acids discharge this, but ammonia restores it.

Metallic Salts.—An aqueous solution of glycocoll will dissolve many metallic oxides, forming salts. Of these, the *copper salt*, $(C_2H_4NO_2)_2Cu + H_2O$, is very characteristic. It crystallizes in dark blue needles. The *silver salt*, $C_2H_4NO_2Ag$, crystallizes on standing over sulphuric acid. The combinations of glycocoll with salts, *e. g.*, $C_2H_5NO_2 . NO_3K$, $C_2H_5NO_2 . NO_3Ag$, are mostly crystalline.

Ammonium Salts.—Glycocoll yields the following compounds with hydrochloric acid: $C_2H_5NO_2 . HCl$ and $2(C_2H_5NO_2) . HCl$. The first is obtained with an excess of hydrochloric acid. It crystallizes in long prisms. The *nitrate*, $C_2H_5NO_2 . HNO_3$, forms large prisms.

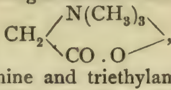
Esters.—The glycocoll esters claim special mention, as they are the starting-out material for the preparation of diazo-acetic esters (p. 365).

The *ethyl ester*, $CH_2{<}\begin{smallmatrix}NH_2\\ CO_2 . C_2H_5\end{smallmatrix}$, is an oil with an odor resembling that of cacao, and boiling at 149°. See glycin anhydride or diglycoldi-imide. On leading HCl gas into glycocoll and absolute alcohol, the HCl-salt is formed; this melts at 144° (B. 21, R. 253).

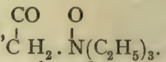
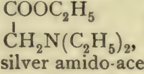
It is also produced when HCl is conducted into alcohol and aceturic acid (p. 356) (B. 29, 760), or by the action of alcoholic hydrochloric acid upon methylene amidoacetonitrile (p. 356). Silver nitrite produces the nitrite salt, $NOOH . NH_2COOC_2H_5$, which readily passes quantitatively into *diazo-acetic ester*, $CH : N_2CO_2C_2H_5$.

Amides.—*Glycocollamide*, $CH_2{<}\begin{smallmatrix}NH_2\\ CO_2NH_2\end{smallmatrix}$, amidoacetamide, is produced when glycocoll is heated with alcoholic ammonia to 160°. A white mass which dissolves readily in water, and reacts strongly alkaline. The HCl-salt results on heating chloracetic ester to 70° with alcoholic ammonia.

Methyl-glycocoll, $CH_2{<}\begin{smallmatrix}NH . CH_3\\ CO_2H\end{smallmatrix}$, or $\begin{array}{l}COO\diagdown\\ |\\ CH_2 . NH_2 . CH_3\end{array}$, **Sarcosine.** Liebig (1847) first obtained it as a decomposition product of the creatine contained in beef extract. Its name is derived from σάρξ, flesh. Volhard (1862) prepared it synthetically by the action of methylamine upon monochloracetic acid and it is also produced when creatine or methyl glycocyamine, $\begin{array}{l}CO_2H \qquad\quad NH_2\\ | \qquad\qquad\quad |\\ CH_2N(CH_3) . C = NH\end{array}$, and caffeine are heated with baryta. It dissolves readily in water but with difficulty in alcohol. The nitrile of sarcosine is obtained together with methylamine from methylene cyanhydrin, the additive product of formaldehyde and prussic acid (A. 279, 39). It melts at 210–220°, decomposing into carbon dioxide and dimethylamine, yielding at the same time diglycolyl dimethylamide. It forms salts with acids; these have an acid reaction. Ignited with soda-lime it evolves methylamine. Sarcosine yields methylhydantoïn with cyanogen chloride and creatine with cyanamide.

Trimethylglycocoll,  $\mathrm{CH_2}\langle\begin{smallmatrix}\mathrm{N(CH_3)_3}\\ \mathrm{CO\,.\,O}\end{smallmatrix}\rangle$, is betaïne, described p. 310.

Ethylamine, diethylamine and triethylamine, acting upon chloracetic acid, produce the ethylated glycocolls in the form of hydrochlorides:

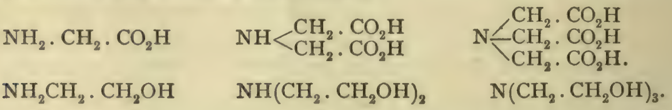
Ethyl-glycocoll, Diethyl-glycocoll and **Triethyl-glycocoll,**  $\begin{matrix}\mathrm{CO} & \mathrm{O}\\ | & |\\ \mathrm{C\,H_2} & .\,\mathrm{N(C_2H_5)_3}\end{matrix}$. The latter boils with decomposition at 210–220°, and differs from the *ethyl ester* of *diethylamidoacetic acid,*  $\begin{matrix}\mathrm{COOC_2H_5}\\ |\\ \mathrm{CH_2N(C_2H_5)_2}\end{matrix}$, boiling at 177°, and resulting from the action of ethyl iodide upon silver amido-acetate (A. **182,** 176).

Methylene Amido-acetonitrile, $\mathrm{CH_2 = N\,.\,CH_2CN}$, melting at 129° with decomposition, is formed from formaldehyde and ammonium cyanide (B. **27,** 59).

Aceto-glycocoll, $\mathrm{CH_2}<\begin{smallmatrix}\mathrm{NH\,.\,C_2H_3O}\\ \mathrm{CO_2H}\end{smallmatrix}$, acetamido-acetic acid, aceturic acid, is obtained by the action of acetyl chloride upon glycocoll silver, and of acetamide upon monochloracetic acid. It dissolves readily in water and alcohol, and melts at 206°. It conducts itself like a monobasic acid (B. **17,** 1664).

Hippuric acid or benzoyl glycocoll (see this) and glycocholic acid (see this), already mentioned under glycocoll, are far more important and will be discussed later. They are constituted like aceturic acid.

Diglycolamidic and triglycolamidic acids bear the same relation to glycocoll that di- and trioxyethylamine sustain to oxethylamine:



$$\mathrm{NH_2\,.\,CH_2\,.\,CO_2H} \qquad \mathrm{NH}<\begin{smallmatrix}\mathrm{CH_2\,.\,CO_2H}\\ \mathrm{CH_2\,.\,CO_2H}\end{smallmatrix} \qquad \mathrm{N}\begin{cases}\mathrm{CH_2\,.\,CO_2H}\\ \mathrm{CH_2\,.\,CO_2H}\\ \mathrm{CH_2\,.\,CO_2H.}\end{cases}$$

$$\mathrm{NH_2CH_2\,.\,CH_2OH} \qquad \mathrm{NH(CH_2\,.\,CH_2OH)_2} \qquad \mathrm{N(CH_2\,.\,CH_2OH)_3.}$$

These compounds are formed on boiling monochloracetic acid with concentrated aqueous ammonia (A. **122,** 269; **145,** 49; **149,** 88).

Diglycolamidic Acid, $\mathrm{NH(CH_2CO_2H)_2}$, melts at 225°, and forms salts both with acids and bases, while *Triglycolamidic Acid,* $\mathrm{N(CH_2CO_2H)_3}$, cannot unite with acids.

Imidoacetonitrile, $\mathrm{NH(CH_2CN)_2}$, melting at 75°, and *Nitriloacetonitrile,* $\mathrm{N(CH_2CN)_3}$, melting at 126°, are obtained from methylene cyanhydrin and ammonia (A. **278,** 229; **279,** 39).

α-**Amidopropionic Acid,** $\mathrm{CH_3\,.\,CH(NH_2)\,.\,CO_2H}$, or $\mathrm{CH_3\,.\,CH\,.(\overline{NH_3)COO}}$, **Alanine,** is derived from *α*-chlor- and *α*-brom-propionic acid by means of ammonia, and from aldehyde ammonia by the action of $\mathrm{CNNH_4}$ and HCl (p. 193). Aggregated, hard needles, with a sweetish taste. The acid dissolves in 5 parts of cold water and with more difficulty in alcohol; in ether it is insoluble. When heated it commences to char at about 237°, melts at 255° and then sublimes. It is partially decomposed into ethylamine and carbon dioxide and in part into aldehyde, carbon monoxide and ammonia (B. **25**, 3502). Nitrous acid converts it into α-lactic acid.

Isomeric β-amido-propionic acid will be treated as the first β-amido-carboxylic acid, p. 358.

Higher homologous α-amido-acids have been mainly prepared by the general methods: (1) By the action of ammonia upon the α-halogen fatty acids, or (2) upon the nitriles of the α-oxy-acids.

α-**Amido-n-butyric Acid**, $CH_3 . CH_2 . CH(NH_2) . CO_2H$.

α-**Amidoisobutyric Acid**, $(CH_3)_2C(NH_2) . CO_2H$, is also produced in the oxidation of diacetonamine sulphate.

α-**Amido-valeric Acid**, $CH_3 . CH_2 . CH_2CH(NH_2) . CO_2H$, is also produced by the oxidation of conine (B. **19**, 500).

α-**Amido-isovaleric Acid**, $(CH_3)_2 . CH . CH(NH_2) . CO_2H$, **Butalanine**, occurs in the pancreas of the ox.

α-**Amidocaproic Acids, Leucines.**—Different α-amido-caproic acids have been described under the name **leucine**. Leucine (from λευκός, glistening white, referring to the appearance of the scaly crystals) occurs in different animal fluids. Its occurrence is physiologically very important. It is present in the pancreas, in the spleen, in the lymph-glands, and in typhoid it is found in the liver. It is formed by the decay of albuminoids, or when they are boiled with alkalies and acids. Fibrin is converted into it by pancreatic digestion (B. **27**, 2727). Horn or dried neck-band of oxen, when treated with dilute sulphuric acid to 100° yields *animal leucine*. Strecker (1848) showed that when it was treated with nitrous acid it passed into an oxy-caproic acid, melting at 73°—probably α-oxy-n-caproic acid—*leucic acid*, p. 337.

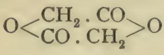
Animal leucine crystallizes in shining leaflets, which have a fatty feel, melt at 270° and sublime undecomposed when carefully heated. Rapid heating breaks it up into amylamine and CO_2. It is soluble in 48 parts of water at 12° and in 800 parts of alcohol.

Vegetable leucine from conglutin, the globulin substance of the *lupines*, is different from the preceding body. It is optically active; the free amido-acid is lævo-rotatory in solution, while its hydrochloride is dextro-rotatory. This leucine becomes optically inactive when it is heated to 160° with baryta water. It is then identical with α-amido-isocaproic acid, $(CH_3)_2 . CH . CH_2 . CH(NH_2) . COOH$, prepared synthetically from isovaleric aldehyde, $(CH_3)_2 . CHCH_2 . CHO$. Nitrous acid converts both acids into α-oxy-isocaproic acid, $(CH_3)_2 . CHCH_2CH(OH)CO_2H$, melting at 54° (p. 337). Penicillium glaucum converts inactive α-amido-isocaproic acid into optically active *dextro-leucine*; the free amido-acid being dextro-rotatory in solution and its hydrochloride lævo-rotatory (B. **24**, 669; **26**, 56). Therefore, the three modifications of α-amido-iso-caproic acid are known.

α-Amido-œnanthic Acid, $CH_3(CH_2)_4CH(NH_2)CO_2H$ (B. **8**, 1168). *α-Amido-caprylic Acid*, $CH_3(CH_2)_5CH(NH_2)CO_2H$ (A. **176**, 344). *α-Amidopalmitic Acid*, $CH_3(CH_2)_{13}CH(NH_2)CO_2H$ (B. **24**, 941). *α-Amidostearic Acid*, $CH_3(CH_2)_{15}CH(NH_2) . CO_2H$, melts at 221° (B. **24**, 2395).

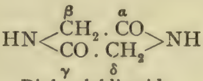
Cyclic Double-acid amides of the α-Amido Carboxylic Acids, αγ-Diacipiperazines. In the formation of esters of the *α*-oxyacids by the action of the carboxyl group and the alcoholic hydroxyl group two molecules enter the reaction. This is also the case in the amide-formation between the carboxyl group and the amido-group of the *α*-amido-acids. Cyclic double-acid amides correspond to the cyclic double esters or lactides.

Diethylenediamine, Piperazine or Hexahydropyrazine (p. 314), is the starting-out substance from which such bodies can be obtained as oxygen substitution products. Hence we have names such as *αγ*-diketo-, *αγ*-diaci-, *αγ*-dioxypiperazine, by means of which we can distinguish the four carbon atoms of the piperazine ring, as *α*-, *β*-, *γ*-, and *δ*-carbon atom:



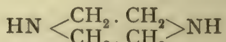
$$O<\begin{matrix}CH_2.CO\\CO.CH_2\end{matrix}>O$$

Diglycollide



$$HN<\begin{matrix}\overset{\beta}{CH_2}.\overset{\alpha}{CO}\\\underset{\gamma}{CO}.\underset{\delta}{CH_2}\end{matrix}>NH$$

Diglycolyldiamide,
αγ-Diacipiperazine



$$HN<\begin{matrix}CH_2.CH_2\\CH_2.CH_2\end{matrix}>NH$$

Diethylenediamine,
Piperazine.

The aromatic piperazine derivatives are particularly numerous (B. **25**, 2941).

Diglycolyldiamide, Glycin Anhydride, *αγ*-Diacipiperazine, $HN<\begin{smallmatrix}CH_2.CO\\CO.CH_2\end{smallmatrix}>NH$, turns brown at 245°, melts at 275°, and is formed when amido-acetic ethyl ester is evaporated with water (B. **23**, 3041).

Diglycolyldimethylamide, Sarcosine Anhydride, $CH_3N<\begin{smallmatrix}CH_2.CO\\CO.CH_2\end{smallmatrix}>N.CH_3$, melting at 150° and boiling at 350°, is produced by heating sarcosine (B. **17**, 286).

Dilactyldiamide, Lactimide, $HN<\begin{smallmatrix}CH(CH_3).CO\\CO.CH(CH_3)\end{smallmatrix}>NH$, melting at 275°, is formed when alanine is heated with hydrochloric acid gas at 180–200° (A. **134**, 372).

β-Amido-carboxylic Acids.

Neither cyclic double-acid amides, such as are obtained from the *α*-amidocarboxylic acids, nor cyclic simple acid amides or lactams, such as are obtained from the *γ*- and *δ*-amidocarboxylic acid, can be prepared from the poorly studied *β*-amidocarboxylic acids.

β-Amidopropionic Acid, *β*-Alanine, $CH_2(NH_2).CH_2.CO_2H$, melts at 196° and breaks down into ammonia and acrylic acid. It is isomeric with alanine (p. 356) and is obtained from *β*-iodpropionic acid with ammonia from *β*-nitropropionic acid, and also from succinimide and succinbromimide by means of bromine and caustic potash (B. **26**, R. 96).

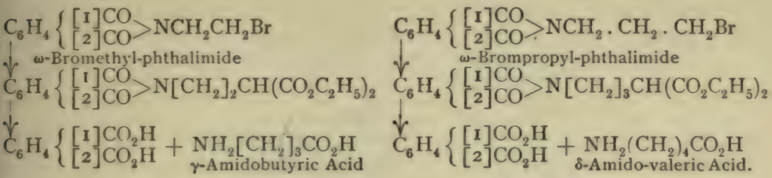
β-Amidobutyric Acid, $CH_3.CH(NH_2).CH_2.CO_2H$(?), is produced when crotonic acid is heated with ammonia (B. **21**, R. 523).

β-Amido-isovaleric Acid, $(CH_3)_2C(NH_2).CH_2.CO_2H$, is obtained by the reduction of the corresponding nitro-acid (p. 350).

γ- and *δ*-Amido-carboxylic Acids.

The most important characteristic of the *γ*- and *δ*-amido-carboxylic acids is that when heated they part with water and yield cyclic, simple acid amides or lactams, the *γ-lactams* and the *δ-lactams*.

Piperidine derivatives, when oxidized, have yielded some of these acids (Schotten). Potassium phthalimide affords a general synthetic method. Ethylene bromide or trimethylene bromide acted upon by it changes to *ω*-bromethyl-phthalimide and *ω*-brompropyl-phthalimide (Gabriel). These bodies, as is known, have also been utilized in the preparation of oxalkylamines (p. 309). In order to get *γ*- and *δ*-amido-carboxylic acids by their aid they are transposed with sodium malonic ester and sodium alkylmalonic ester. The condensation product resulting in this manner is decomposed, on heating it with hydrochloric acid, into phthalic acid, γ-, or δ-amido carboxylic hydrochloride, carbon dioxide and alcohol (B. **24**, 2450):



$$C_6H_4\left\{\begin{array}{l}{[1]}CO\\ {[2]}CO\end{array}\right> NCH_2CH_2Br \qquad C_6H_4\left\{\begin{array}{l}{[1]}CO\\ {[2]}CO\end{array}\right> NCH_2 . CH_2 . CH_2Br$$

$$\downarrow \text{ ω-Bromethyl-phthalimide} \qquad \downarrow \text{ ω-Brompropyl-phthalimide}$$

$$C_6H_4\left\{\begin{array}{l}{[1]}CO\\ {[2]}CO\end{array}\right> N[CH_2]_2CH(CO_2C_2H_5)_2 \qquad C_6H_4\left\{\begin{array}{l}{[1]}CO\\ {[2]}CO\end{array}\right> N[CH_2]_3CH(CO_2C_2H_5)_2$$

$$\downarrow \qquad \downarrow$$

$$C_6H_4\left\{\begin{array}{l}{[1]}CO_2H\\ {[2]}CO_2H\end{array}\right. + \underset{\gamma\text{-Amidobutyric Acid}}{NH_2[CH_2]_3CO_2H} \qquad C_6H_4\left\{\begin{array}{l}{[1]}CO_2H\\ {[2]}CO_2H\end{array}\right. + \underset{\delta\text{-Amido-valeric Acid.}}{NH_2(CH_2)_4CO_2H}$$

γ-Amidobutyric Acid, Piperidic Acid, melts at 183–184° and loses water. It is formed (1) when piperidylurethane, $CH_2<\begin{array}{l}CH_2 . CH_2\\ CH_2 . CH_2\end{array}>N . CO_2C_2H_5$, is oxidized with nitric acid (B. **16**, 644); (2) by means of potassium phthalimide; either—(a) by the double decomposition of brom-ethyl phthalimide with sodium malonic ester (see above), or (b) by transposing ω-brompropyl-phthalimide with potassium cyanide, and decomposing the phthalyl-γ-amidobutyric nitrile (B. **23**, 1772).

γ-Amidovaleric Acid, $CH_3 . CH(NH_2) . CH_2 . CH_2 . CO_2H$, results from the decomposition of phenylhydrazone-lævulinic acid by sodium amalgam (B. **27**, 2313). It melts at 193°. Both γ-amido-acids, when heated, pass into lactams.

δ-Amido-n-valeric Acid, $NH_2(CH_2)_4 . CO_2H$ (Homopiperidic Acid), melts at 158°. Its benzoyl derivative and *sulpho-δ-amido-valeric acid*, $SO_2[NH(CH_2)_4\text{-}CO_2H]_2$, melting at 163°, are formed when benzoyl piperidine,

$$CH_2<\begin{array}{l}CH_2 . CH_2\\ CH_2 . CH_2\end{array}>N . COC_6H_5,$$

and sulphopiperidine are oxidized with $KMnO_4$ (B. **21**, 2240). The acid results from phthalyl propyl malonic diethyl ester (B. **23**, 1769). In the latter manner the following acids have been prepared: a-Methyl-δ-amido-n-valeric acid, $NH_2 . CH_2 . CH_2 . CH_2 . CH(CH_3)CO_2H$, melting at 168°; a-Ethyl-δ-amido-n-valeric acid, $NH_2 . CH_2 . CH_2 . CH_2 . CH(C_2H_5)CO_2H$, melting at 200–200.5°; a-Propyl-δ-amido-n-valeric acid, $NH_2 . CH_2 . CH_2 . CH_2 . CH(C_3H_7)CO_2H$, melting at 186° (B. **24**, 2444). *δ-Amido-n-Octanic Acid*, Homoconinic acid, $C_3H_7 . CH(NH_2) . CH_2 . CH_2 . CH_2 . CO_2H$, melts at 158°. Its benzoyl derivative is produced when benzoyl conine is oxidized with potassium permanganate (B. **19**, 502).

γ- and δ-Lactams: Cyclic Amides of the γ- and δ-Amidocarboxylic Acids.

These bodies are formed when the γ- and δ-amido-acids are heated to their point of fusion. They then lose water, and suffer an intramolecular condensation. Some of them have been obtained by the reduction of the anilchlorides of dibasic acids—*e. g.*, dichlormaleïn anilchloride. They correspond to the γ- and δ-lactones. The names γ-lactams and δ-lactams have been given them to recall the lactones. They are cyclic acid-amides. Just as the lactones, under the influence of the caustic alkalies, yield oxy-acid salts, so the lactams, when digested with alkalies or acids, pass into salts of the amido-acids, from which they can be formed on the application of heat.

Further, the γ- and δ-lactams bear the same relation to the imides of the γ- and δ-alkylen diamines as the lactones sustain to the oxides of the γ- and δ-glycols (p. 343). These relations are apparent in the following arrangement:

$\begin{array}{l}CH_2 . CH_2OH\\ \vert\\ CH_2 . CH_2OH\end{array}$ Tetramethylene Glycol	$\begin{array}{l}CH_2 . CH_2 . NH_2\\ \vert\\ CH_2 . CH_2 . NH_2\end{array}$ Tetramethylene Diamine	$CH_2<\begin{array}{l}CH_2 . CH_2OH\\ CH_2CH_2OH\end{array}$ Pentamethylene Glycol	$CH_2<\begin{array}{l}CH_2 . CH_2 . NH_2\\ CH_2 . CH_2 . NH_2\end{array}$ Pentamethylene Diamine
$\left.\begin{array}{l}CH_2 . CH_2\\ \vert\\ CH_2 . CH_2\end{array}\right>O$ Tetramethylene Oxide, Tetrahydrofurfurane	$\left.\begin{array}{l}CH_2 . CH_2\\ \vert\\ CH_2 . CH_2\end{array}\right>NH$ Tetramethylene Imide, Tetrahydropyrrol	$CH_2<\left.\begin{array}{l}CH_2 . CH_2\\ CH_2 . CH_2\end{array}\right>O$ Pentamethylene Oxide	$CH_2<\left.\begin{array}{l}CH_2 . CH_2\\ CH_2 . CH_2\end{array}\right>NH$ Pentamethylene Imide, Piperidine
$\left.\begin{array}{l}CH_2 . CO\\ \vert\\ CH_2 . CH_2\end{array}\right>O$ γ-Butyrolactone	$\left.\begin{array}{l}CH_2 . CO\\ \vert\\ CH_2 . CH_2\end{array}\right>NH$ γ-Butyrolactam, α-Pyrrolidone	$CH_2<\left.\begin{array}{l}CH_2 . CO\\ CH_2 . CH_2\end{array}\right>O$ δ-Valerolactone	$CH_2<\left.\begin{array}{l}CH_2 . CO\\ CH_2 . CH_2\end{array}\right>NH$ δ-Valerolactam, α-Oxopiperidine, α-Piperidone.

γ-**Lactams**: γ-*Butyrolactam*, α-Pyrrolidone, $\left.\begin{array}{l}CH_2 . CO\\ \vert\\ CH_2 . CH_2\end{array}\right>NH$, melting at 25° to 28° and boiling at 245°, unites with water to a crystalline hydrate, $C_4H_7ON + H_2O$, melting at 35°. n-*Phenyl-γ-butyrolactam* is produced in the reduction of dichlormaleïn anilchloride (B. **28**, 58). γ-*Valerolactam*, δ-methyl pyrrolidone, $\left.\begin{array}{l}CH_2 - CH(CH_3)\\ \vert\\ CH_2 \text{———} CO\end{array}\right>NH$, melting at 37° and distilling without decomposition, is reduced by amyl alcohol and sodium to *α-methyl pyrrolidine* (p. 315) (B. **22**, 1860, 3338, 2364; **23**, 708).

δ-**Lactams**: δ-*Valerolactam*, α-Ketopiperidine, α-Oxopiperidine, α-Piperidone, $CH_2<\left.\begin{array}{l}CH_2 . CO\\ CH_2 . CH_2\end{array}\right>NH$, melts at 39–40° and boils at 256° (B. **21**, 2242). *α-Methyl-δ-valerolactam*, β-Methyl Piperidone, $CH_2<\left.\begin{array}{l}CH(CH_3)CO\\ CH_2 - CH_2\end{array}\right>NH$, melts at 53.5° to 55°. *α-Ethyl-δ-valerolactam*, β-Ethyl Piperidone, $CH_2<\left.\begin{array}{l}CH(C_2H_5)CO\\ CH_2 \text{——} CH_2\end{array}\right>NH$, melts at 68° and boils at 140–142° (42 mm.) (B. **23**, 3694). *α-Propyl-δ-valerolactam*, β-Propyl Piperidone, $CH_2<\left.\begin{array}{l}CH(C_3H_7)CO\\ CH_2 \text{——} CH_2\end{array}\right>NH$, melts at 59° and boils at 274°. δ-n-*Octanolactam*, Homoconinic Acid Lactam, $CH_2<\left.\begin{array}{l}CH_2CO\\ CH_2 . CH - C_3H_7\end{array}\right>NH$, melts at 84°.

The amido-acids are not poisonous, but their γ- and δ-lactams are violent, strychnine-like poisons, affecting the spinal cord and producing cramps. We shall again meet these bodies under the pyrrol and pyridine derivatives, where they will appear as tetrahydropyrrol and piperidine compounds.

9. **Fatty Acid Nitramines**, *Nitramine-acetic Acid*, $CO_2H . CH_2 . NH . NO_2$(?), melting at 103°, is prepared by saponifying its ethyl ester (melting at 24°), which results on treating nitrourethane acetic ester, $CO_2C_2H_5 . CH_2N(NO_2)CO_2C_2H_5$, with ammonia (B. **29**, 1682).

10. **Isonitramine Fatty Acids** are obtained in the form of their sodium salts when sodium isonitramine acetoacetic esters and sodium isonitramine-mono-alkyl acetoacetic esters are acted upon by the alkalies (B. **29**, 667). They are converted into amidoxy-fatty acids by dilute mineral acids (p. 350). Acid reducing agents change them to amino-fatty acids, while alkaline reducing agents produce diazo-acids (p. 365) and hydrazino-acids (see below).

Isonitramine-acetic Acid, $CO_2H\,.\,CH_2N{<}\begin{matrix}O\\ |\\ N{-}OH\end{matrix}$, and its homologues are syrupy, easily decomposable liquids. Their lead salts dissolve with difficulty.

11 (*a*). **Hydrazino-fatty Acids** are obtained, together with the diazo-acids, when the isonitramine-fatty acids are acted upon with alkaline reducing agents. Their carbamide derivatives are obtained in the form of nitriles when prussic acid adds itself to the ketone semicarbazides. *a-Hydrazino-propionic Acid*, Amido-alanine, NH_2,-$NH\,.\,CH(CH_3)CO_2H$, melting at 180°, is formed from a-isonitramine propionic acid (B. **29**, 670). *a-Hydrazinobutyric Acid*, $NH_2\,.\,NH\,.\,C(CH_3)_2CO_2H$, melts, with decomposition, at 237°. It is formed when steam acts upon its benzal derivative. The latter is made by acting on acetone semi-carbazide, $NH_2CO\,.\,NH\,.\,N = C(CH_3)_2$, with prussic acid, when carbonamid-hydrazino-isobutyronitrile is produced. This is then decomposed with hydrochloric acid, and benzaldehyde is added (A. **290**, 15).

s-*Phenylhydrazino-acetic Acid*, $C_6H_5NH\,.\,NH\,.\,CH_2\,.\,CO_2H$, melting at 158°, is produced by the careful reduction of phenylhydrazone-glyoxylic acid, and when chloracetic acid acts upon phenylhydrazine (B. **28**, 1230). unsym.-*Phenylhydrazino-acetic Acid*, $C_6H_5N(NH_2)CH_2\,.\,CO_2H$, melts, with decomposition at 167° (B. **28**, 1226).

11 (*b*). **Hydrazo-fatty Acids.**—When a hydrazino-fatty acid is treated with acetone and potassium cyanide, a hydrazo-nitrile acid results: thus, from a-hydrazino-isobutyric acid we get *hydrazo-isobutyro-nitrilic acid*, $(CH_3)_2C{<}\begin{matrix}NH & \text{—} & NH\\ CO_2H & & CN\end{matrix}{>}C(CH_3)_2$, melting at 100°. When hydrazine sulphate (1 mol.), acetone (2 mols.), and potassium cyanide (2 mols.) react, the product is *Hydrazo-isobutyronitrile*, $(CH_3)_2C{<}\begin{matrix}NH & \text{—} & NH\\ CN & & CN\end{matrix}{>}C$-$(CH_3)_2$, melting at 92°. Hydrochloric acid converts both nitriles into *Hydrazo-isobutyric Acid*, $(CH_3)_2C{<}\begin{matrix}NH & \text{——} & NH\\ CO_2H & & CO_2H\end{matrix}{>}C(CH_3)_2$, melting at 223° (A. **290**, 1).

12. **Azo-fatty Acids.**—Bromine water oxidizes hydrazo-esters and hydrazonitriles to the corresponding azo-bodies. **Azo-isobutyronitrile,** $(CH_3)_2C{<}\begin{matrix}N & = & N\\ CN & & CN\end{matrix}{>}C$-$(CH_3)_2$, melting at 105°, when heated alone, or, better, with hot water, passes into tetramethyl succinic nitrile (A. **290**, 1).

B. UNSATURATED OXY-ACIDS, OXY-OLEFINE CARBOXYLIC ACIDS.

The a-acids are formed when their nitriles, the additive products arising from hydrocyanic acid and unsaturated aldehydes, are treated with cold hydrochloric acid. When boiled with dilute hydrochloric acid, the a-oxy-$\Delta\beta\gamma$-unsaturated acids are rearranged into γ-ketone carboxylic acids (Fittig, B. **29**, 2582)—*e. g.*, crotonaldehyde yields:

$$\underset{a\text{-Oxy-pentenic Acid}}{CH_3\,.\,CH : CH\,.\,CH{<}\begin{matrix}CO_2H\\ OH\end{matrix}}\text{, which passes into }\underset{\text{Lævulinic Acid.}}{CH_3\,.\,CO\,.\,CH_2\,.\,CH_2\,.\,CO_2H}$$

β-Oxy-unsaturated Acids.—Oxy-methylene acetic acid, formerly called formyl-acetic acid, must be considered an unsaturated β-oxy-acid (compare oxy-methylene acetone, p. 319).

β-Oxy-acrylic Acid, Formyl Acetic Acid, Oxy-methylene Acetic Acid, $HO\,.\,CH = CH\,.\,CO_2H$ (early formula, $CHO\,.\,CH_2\,.\,CO_2H$). Its ester is formed by the condensation of acetic ester with formic ester. Metallic sodium is used for this purpose. It readily condenses to trimesic ester or benzene-1.3.5-tricarboxylic ester, C_6H_3-$(CO_2C_2H_5)_3$ (B. **21**, 1146). The sodium compound of the β-oxy-acrylic ester combines with acetyl chloride to the acetate $CH(OCOCH_3) : CH\,.\,CO_2C_2H_5$, boiling at 126° (under 46 mm.), which bromine changes to the *acetate* of *$a\beta$-Dibrom-β-oxy-*

propionic ester, $CH_3 . CO . OCHBr . CHBr . CO_2C_2H_5$, boiling at 153–154° (34 mm). This reveals the constitution of the acetate (B. **25**, 1040). Concentrated sulphuric acid converts formyl acetic acid into *coumalic acid* (see this).

α-Oxymethylene-propionic Ester, methyl-formyl acetic ester, $HO . CH : C(CH_3) . CO_2C_2H_5$, boils at 160–162°. Its *acetate* boils at 132° (48 mm.). *β-Oxyisocrotonic Acid*, $CH_3 . C(OH) = CH . CO_2H$, is not known, but its ketoform, acetoacetic acid, is known.

The following bodies must be regarded as derivatives of β-oxycrotonic acid: *β-Methoxy*(trans)*isocrotonic Acid*, $CH_3 . C(O . CH_3) : CH . CO_2H$, melting at 128.5°, may be obtained by the action of sodium ethylate upon β-chlorisocrotonic ethyl ester (p. 280) (A. **219**, 344). *β-Methoxy*(trans)*isocrotonic Ethyl Ester*, from β-chloriso-crotonic ethyl ester and sodium methylate (A. **256**, 207), boils at 178°. *β-Methoxy*-(cis)*isocrotonic Ethyl Ester*, from acetoacetic ester and diazomethane in ether, boils at 188°. Both esters on saponification yield the same β-methoxy(trans)isocrotonic acid (B. **28**, 1626). *β-Ethoxy-isocrotonic Ethyl Ester*, $CH_3C(OC_2H_5) : CH . CO_2C_2H_5$, melting at 30° and boiling at 195°, is also formed when acetyl chloride is allowed to act upon a mixture of acetoacetic ester and orthoformic ester (B. **26**, 2729). The free acid is obtained by its saponification, and on splitting off carbon dioxide yields isopropylene ethyl ether (p. 136).

β-Oxycrotonic acid derivatives are also formed when sodium acetoacetic ester is treated with $Cl . COOC_2H_5$, CH_3COCl, and C_6H_5COCl (see p. 377). *β-Carbethoxyl-oxycrotonic Ester*, $CH_3 . C(OCO_2C_2H_5) = CHCO_2C_2H_5$, boils at 131° (14 mm.) (B. **25**, 1760). *β-Acetyl-oxycrotonic Ester*, $CH_3 . C(OC . OCH_3) : CHCO_2C_2H_5$, boils at 98° (12 mm.). *β Benzoyl-oxycrotonic Ester*, $CH_3 . C(OCOC_6H_5) = CHCO_2C_2H_5$, melts at 43°. In contrast to the isomerides, in which the three acid radicals are attached to the α-carbon atom, the β-oxycrotonic esters do *not* dissolve in the alkalies. Alcoholates cause them to revert to acetoacetic ester. At low temperatures they take up bromine. Their formation from sodium acetoacetic ester argues for the formula $CH_3 . C(ONa) : CH . CO_2C_2H_5$ of the latter (p. 372).

γ- and δ-Oxyolefine acids are known in the form of their lactones; some of them have been prepared by the distillation of γ-ketonic acids: thus, lævulinic and acetyl lævulinic (p. 379) acids yield:

α-Angelica lactone, $CH_3 . C : CH . CH_2COO$, melting at 18° and boiling at 167°.

β-Angelica lactone, $CH_2 : C — CH_2 . CH_2COO$, boiling at 83° (25 mm.), gradually changes, when distilled under ordinary pressure, into α-angelica lactone.

Parasorbic Acid, or Sorbin Oil, $CH_3 . CH_2 . CH . CH : CH . COO$, or $CH_3 . CH . CH_2 . CH : CH . COO$, boiling at 221°, occurs, together with malic acid, in the juice of ripe and unripe mountain ash berries (*Sorbus aucuparia*). It is optically active: $[\alpha]j = + 40.8$, and is an energetic emetic. It passes into sorbic acid (p. 289) when heated with sodium hydroxide or hydrochloric acid (B. **27**, 344). Mesitonic acid (p. 381) yields *α-Dimethyl-α-angelica lactone*, melting at 24° and boiling at 167°.

Unsaturated δ-lactones have been obtained from coumalic acid and isodehydracetic acid by the splitting-off of carbon dioxide:

Coumalin, $CH = CH — CH = CH . COO$, melting at + 5° and boiling at 120° C. (30 mm.), has an odor like that of coumarin (A. **264**, 293).

Mesitene Lactone, βδ-Dimethyl-coumalin, $CH_3C = CH — C(CH_3) = CH . COO$, melts at 51.5° and boils at 245°. When heated with ammonia it changes to the corresponding lactam, so-called *pseudo-lutidostyril*, *mesitene lactam* (p. 363).

Ricinoleic Acid, $C_{18}H_{34}O_3$, is an unsaturated oxy-carboxylic acid (p. 286).

Unsaturated β-Amido-acids and β-Hydrazido-acids.

Esters of unsaturated β-amido-acids are formed when ammonia or primary and secondary amines (B. **18**, 619; **25**, 777) act upon acetoacetic esters and monoalkyl acetoacetic esters.

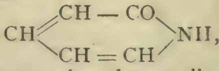
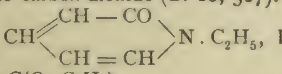
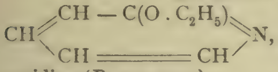
β-Amidocrotonic Ester, $CH_3C(NH_2):CH.CO_2C_2H_5$, boiling at 34°, is produced when ammonia acts upon acetoacetic ester, as well as upon β-chloranticrotonic ester (B. **28**, R. 927). Aqueous hydrochloric acid causes it to revert to acetoacetic ester (A. **236**, 292), while dry hydrogen chloride produces a salt, which at 130° is rearranged into ammonium chloride, and the ester of an unsaturated δ-lactam-carboxylic acid—*pseudo-lutidostyril carboxylic acid* (B. **20**, 445; A. **259**, 172). For the effect of heat upon the free ester consult B. **28**, R. 603.

β-Anilidocrotonic Ester, $CH_3C(NHC_6H_5) = CH.CO_2C_2H_5$, a thick oil, distils undecomposed under reduced pressure, and when heated to 200° at the ordinary pressure is condensed to *γ-oxyquinaldine* and phenyl-lutidone carboxylic acid (B. **20**, 947, 1398).

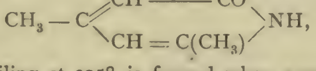
These derivatives of β-amido-crotonic acid manifest no inclination towards the formation of simple, cyclic β-lactams, but when they condense through the interaction of two molecules, bodies of complex constitution result. The conditions, however, immediately change when *hydrazine* and *phenylhydrazine* are substituted for ammonia and ammonia bases in the reaction with acetoacetic esters. The tendency on the part of the resulting primary β-hydrazido-crotonic acid derivatives to lactam formation is exceedingly great. The products have been called pyrazolon-derivatives. *Antipyrine* belongs to this class. Should it seem desirable to introduce a special name for these lactams, in which the lactam-nitrogen is joined to a second nitrogen atom, they might be designated *lactazams*. Thus, β-hydrazido-crotonic ester loses alcohol and passes easily into the corresponding lactazam—3-methyl-pyrazolon:

$$\begin{array}{l} CH_3.C:CH.CO.OC_2H_5 \\ \quad\;\, | \\ \quad NH—NH_2 \end{array} \longrightarrow \begin{array}{l} CH_3.C:CH.CO \\ \quad\;\, | \qquad\quad\; | \\ \quad NH——NH \end{array}$$

Lactams of Unsaturated δ-Amido-acids.

α-Pyridone, [δ-Amino-pentadiēn-lactam] , melting at 106°, is obtained from the reaction product of ammonia and coumalic acid after the elimination of carbon dioxide (B. **18**, 317). It can be converted into the odorless *Ethylimide*, , boiling at 258°, and *α-Ethoxypyridine*, , boiling at 156°, and possessing an odor like that of pyridine (B. **24**, 3144).

Pseudolutidostyril, [3.5]*-dimethyl-α-pyridone*, *mesitene lactam*,



melting at 180° and boiling at 305°, is formed when ammonia acts upon mesitene lactone, and from the two monocarboxylic acids of this lactam by the elimination of CO_2 (A. **259**, 168).

8. ALDEHYDE ACIDS.

These are bodies which show both the properties of a carboxylic acid and of an aldehyde. Formic acid is the simplest representative of the class. and it is also the first member of the homologous series of saturated aliphatic monocarboxylic acids. But it and its derivatives have been, with repeated reference to its aldehydic nature, discussed before acetic acid and their higher homologues. The best known aldehyde carboxylic acid, a compound of the aldehyde group CHO with the carboxyl group COOH, is glyoxylic acid, which is an oxidation product of ethylene glycol.

Glyoxylic Acid, *Glyoxalic Acid* [Ethanal Acid] $(HO)_2 . CH . CO_2H$, was found by Debus (1856) among the products resulting from the oxidation of alcohol with nitric acid. It occurs in the unripe gooseberries. Just as chloral hydrate is to be considered as trichlorethidene glycol, $CCl_3CH(OH)_2$, so crystallized glyoxylic acid can be regarded as the glycol corresponding to the aldehydo-acid, $CHO . CO_2H$. All the salts are derived from the dihydroxyl formula of glyoxylic acid; hence it may be designated dioxy-acetic acid. Like chloral hydrate, glyoxylic acid in many reactions deports itself like a true aldehyde (B. **25**, 3425).

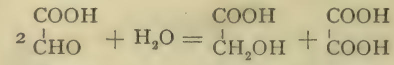
Methods of Formation.—Glyoxylic acid is obtained by (1) oxidizing glycol, alcohol and aldehyde together with glyoxal and glycollic acid; (2) by heating dichlor- and dibrom-acetic acid to 230° with water (B. **25**, 714); (3) by boiling silver dichlor-acetate with water (B. **14**, 578); also from hydrazi-acetic acid (p. 366).

Properties.—It is a thick liquid, readily soluble in water, and crystallizes in rhombic prisms by long standing over sulphuric acid. The crystals have the formula $C_2H_4O_4$. It distils undecomposed with steam.

Salts.—When dried at 100°, the salts have the formula $C_2H_3MeO_4$. The *ammonium salt* alone has the formula $C_2H(NH_4)O_3$. The *calcium salt*, $(C_2H_3O_4)_2Ca$, crystallizes with one and two molecules of water (B. **14**, 585), and is sparingly soluble in water.

Deportment.—Glyoxylic acid manifests all the properties of an aldehyde. It reduces ammoniacal silver solutions with formation of a mirror, and combines with primary alkali sulphites (p. **191**), with phenylhydrazine (B. **17**, 577), with hydroxylamine, thiophenol and hydrochloric acid (B. **25**, 3426). When oxidized (silver oxide), it yields oxalic acid; by reduction it forms glycollic acid and racemic acid, $CO_2H . CH(OH) . CH(OH)COOH$. On boiling the acid with alkalies, glycollic and oxalic acids are produced (B. **13**, 1931).

This reaction is extramolecular. It completes itself by the intramolecular rearrangement of the glyoxal, under like conditions, into glycollic acid:



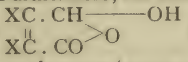
$$2\begin{array}{l}COOH\\|\\CHO\end{array} + H_2O = \begin{array}{l}COOH\\|\\CH_2OH\end{array} + \begin{array}{l}COOH\\|\\COOH\end{array}$$

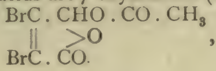
Glyoxylic Acid — Glycollic Acid — Oxalic Acid.

When hydrocyanic and hydrochloric acids act upon glycollic acid, a like transposition ensues. See conversion of urea into allantoin.

The acids obtained by the condensation of formic ester with acetic ester and mono-alkyl acetic esters are unsaturated β-oxy-acids. They were formerly thought to be β-aldehydo-acids. *Formyl Acetic Acid*, $CHO . CH_2 . COOH$, is of this class. *Oxy-methylene Acetic Acid*, $HO . CH : CH . CO_2H$, is another. These oxy-methylene fatty acids have been already described in connection with the oxy-paraffin carboxylic acids (p. 361).

UNSATURATED ALDEHYDO-ACIDS.

Mucochloric Acid, the half-aldehyde of dichlormaleïc acid, $CHO.CCl=CCl.CO_2H$, melting at 125°, and *mucobromic acid*, $CHO.CBr=CBr.CO_2H$, melting at 122° (B 28, 1886), produced in the action of chlorine and bromine upon pyromucic acid, are probably substitution derivatives of the unknown acid $CHO.CH=CH.CO_2H$ (Beilstein, L. Jackson and Hill). Furthermore, the following constitutional formula has been proposed for these acids:  $\begin{array}{l} XC.CH\text{———}OH \\ \| \qquad > O \\ XC.CO \end{array}$ (A. 239, 177). This would seem to indicate that the acids are γ-oxylactones (compare γ-ketone carboxylic acids).

Acetyl Mucobromic Acid,  $\begin{array}{l} BrC.CHO.CO.CH_3 \\ \| \quad > O \\ BrC.CO \end{array}$, melts at 50°.

NITROGEN DERIVATIVES OF THE ALDEHYDO-ACIDS.

Diazoacetic acid, $N_2CH.CO_2H$, is the most remarkable derivative of glyoxylic acid. As it contains two doubly-linked nitrogen atoms, it may be compared to the *aromatic diazo-bodies* (see diazobenzene). However, in the latter the extra affinities of the diazo-group $-N=N-$ or $=N\equiv N$ are combined to two atoms, while in diazoacetic acid they are joined to a single carbon atom,  $\begin{array}{l} N \\ \| > CH.CO_2H. \\ N \end{array}$ Separated by acids from its salts, it undergoes an immediate decomposition, but it is quite stable in its esters and its amides.

The sodium salts of the diazo-acids have been prepared by reducing the isonitramine fatty acids (p. 360) with sodium amalgam (W. Traube, B. 29, 667):

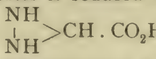
$$HO_2N_2CH_2CO_2H + 2H = 2H_2O + N_2:CH.CO_2H.$$

The esters of the diazo-acids result when potassium nitrite acts upon the hydrochlorides of the amido-fatty acid esters (p. 355) (Curtius, 1883, B. 29, 759):

$$\underset{\substack{\text{Glycocoll Ester} \\ \text{Hydrochloride}}}{HCl.(H_2N)CH_2.CO_2C_2H_5} + NO_2K = \underset{\text{Diazoacetic Ester.}}{N_2:CH.CO_2C_2H_5} + KCl + 2H_2O.$$

The diazo-acids are very volatile, yellow-colored liquids, with peculiar odor. They distil undecomposed with steam, or under reduced pressure. They are slightly soluble in water, but mix readily with alcohol and ether. Like acetoacetic ester, they are feeble acids; the hydrogen of their CHN_2-group can be replaced by alkali metals. This change may be effected by the action of alcoholates. Aqueous alkalies gradually saponify and dissolve them, with the formation of salts, $CHN_2.CO_2Me$. Acids decompose these at once with the evolution of nitrogen. Sodium amalgam reduces them to hydrazino-acids (B. 29, 667).

Sodium diazoacetate, yellow in color, dissolves with extreme ease in water. The reaction of its solution is alkaline.

Ethyl Diazoacetate, $CHN_2.CO_2.C_2H_5$, boils at 143–144° (under 120 mm. pressure); its sp. gr. is 1.073 at 22°. When chilled it solidifies, forming a leafy, crystalline mass, melting at −24°. It explodes with violence when brought in contact with concentrated sulphuric acid. A blow does not have this effect. It is a feeble acid. Its *mercury salt*, $Hg(CN_2 . CO_2 . C_2H_5)_2$, melts with foaming at 104°. It results when yellow mercuric oxide acts upon diazoacetic ester. The mixture should be well cooled. It separates from ether in transparent, sulphur-yellow, rhombic crystals. Concentrated ammonia converts it, like all other esters, into an amide, **diazoacetamide**, $CHN_2 . CO . NH_2$, melting at 114° with decomposition. When diazoacetic ester is reduced it breaks down into ammonia and glycocoll. *Hydrazi-acetic acid*,  $\begin{matrix}NH\\ |\\ NH\end{matrix}\!\!>CH . CO_2H$, stable only in the form of its salts, is an intermediate product. Acids decompose it into hydrazine and glyoxylic acid (B. **27**, 775).

The diazo-compounds of the marsh-gas series are especially reactive. They split off nitrogen, and its place is taken either by *two* univalent atoms or radicals.

(1) The diazo-esters are converted, by boiling water or dilute acids, into esters of the *oxy-fatty acids* (glycol acids, p. 330):

$$CHN_2 . CO_2 . C_2H_5 + H_2O = CH_2(OH) . CO_2 . C_2H_5 + N_2$$

Ester of Glycollic Acid.

This reaction can serve for the quantitative estimation of the nitrogen in diazo-derivatives. (2) Alkyl glycollic esters are produced on boiling with alcohols:

$$CHN_2 . CO_2 . C_2H_5 + C_2H_5 . OH = CH_2(O . C_2H_5) . CO_2 . C_2H_5 + N_2;$$

Ethyl Glycollic Ethyl Ester.

a small quantity of aldehyde is produced at the same time.

(3) Acid derivatives of the glycollic esters are obtained on heating the diazo-compounds with organic acids:

$$CHN_2 . CO_2 . C_2H_5 + \underset{\text{Acetic Acid.}}{C_2H_3O . OH} = \underset{\text{Aceto-glycollic Ester.}}{CH_2(O . C_2H_3O) . CO_2 . C_2H_5} + N_2.$$

(4) The haloid acids act, even in the cold, upon the diazo-compounds. The products are *haloid fatty acids:*

$$CHN_2 . CO_2 . C_2H_5 + HCl = CH_2Cl . CO_2 . C_2H_5 + N_2.$$

(5) The halogens produce esters of dihaloid fatty acids:

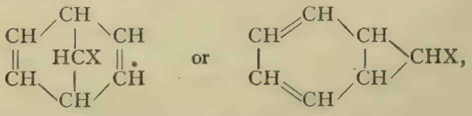
$$CHN_2 . CH_2 . C_2H_5 + I_2 = \underset{\text{Di-iodo-acetic Ester.}}{CHI_2 . CO_2 . C_2H_5} + N_2.$$

Diazo-acetamide is changed, in a similar manner, to di-iodo-acetamide, $CHI_2 . CO . NH_2$. By titration with iodine it is possible to employ this reaction for the quantitative estimation of diazo-fatty compounds (B. **18**, 1285).

(6) The esters of anilido-fatty acids, $C_6H_5 . NH . CH_2 . CO_2R$, result from the union of the anilines with diazo esters. (7) They revert to the amido-acids upon reduction (with zinc dust and glacial acetic acid). Hydrazine-fatty acids are intermediate products. These are not very stable (B. **17**, 957).

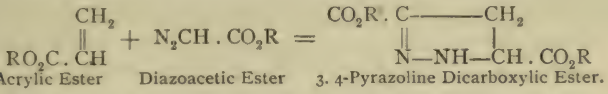
(8) The esters of the diazo-fatty acids unite with aldehydes to form esters of the ketonic acids, *e. g.*, benzoylacetic ester, $C_6H_5 . CO . CH_2 . CO_2 . C_2H_5$ (B. **18**, 2379).

(9) Diazo-acetic ester produces a peculiar ester by its union with benzene. This compound is isomeric with phenyl-acetic ester, $C_6H_5 . CH_2 . CO_2C_2H_5$ (B. **18**, 2377). It probably has one of the following constitutional formulas:

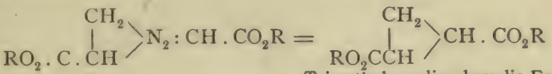


in which X represents the group $CO_2C_2H_5$ (B. **29**, 108).

(10) The diazoacetic esters and the esters of the unsaturated acids (acrylic, cinnamic, fumaric) combine to additive products, which crystallize well:

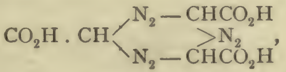


On the application of heat nitrogen is split off, and an ester of trimethylene dicarboxylic acid results:

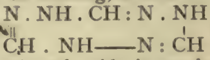

Trimethylene-dicarboxylic Ester.

Starting with diazoacetic esters Curtius obtained *diamide* or *hydrazine*, $NH_2—NH_2$ (B. **27**, 775) and from the latter *hydronitric acid*, N_3H, *hydrazoic acid*.

Triazo-acetic Acid, Triazo-trimethylene-tricarboxylic acid,



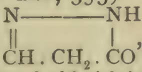
a polymerization product of diazo-acetic acid, is the starting-out material for the preparation of diamide.

Its sodium salt is formed when concentrated sodium hydroxide acts upon diazo-acetic ester; it crystallizes with $3H_2O$ in brilliant, orange-yellow plates, which melt at 152° when rapidly heated (B. **22**, R. 133, 196). The acid is almost insoluble in cold water, ether and benzene, but soluble in alcohol and glacial acetic acid. The sodium salt dissolves with difficulty. The free acid, on heating, breaks down into CO_2 and colorless, crystalline *Trimethine-triazimide*,  (?).

Triazo-acetic acid upon digestion with water or mineral acids is resolved into oxalic acid and **Hydrazine**:

$$C_3H_3N_6(CO_2H)_3 + 6H_2O = 3C_2H_2O_4 + 3N_2H_4.$$

Oximes.—*Oximido-acetic Acid*, $HO.N = CHCO_2H$, melting at 137°, is formed from glyoxylic acid and hydroxylamine, as well as from dichlor- and dibromacetic acid by means of hydroxylamine and caustic potash. *Oximido-acetic Ethyl Ester*, a thick oil, is changed by oxidation to dioxo-succinic-dioxime-peroxide (B. **28**, 1213). *Oximido-acetoacetic Acid*, $CO_2H.CH = NO.CH_2.CO_2H$, melting at 181°, results from oximido-acetic acid and chlor-acetic acid in alkaline solution (A. **289**, 298). *Oximido-acetonitrile Acetate*, $CH_3.CO.ON = CH.CN$, melts at 46° (B. **25**, 912). *β-Oximido-propionic Acid*, $HO.N = CH.CH_2.CO_2H$, melts at 117° with foaming. It is formed when hydroxylamine acts on coumalic acid (A. **264**, 286; B. **25**, 1904). It is the oxime of the half-aldehyde of malonic acid, which, however, is not known, but rearranges itself to oxymethylene acetic acid (p. 361).

Hydrazones.—Phenylhydrazone Glyoxylic Acid, $C_6H_5NHN = CH.CO_2H$, melts with decomposition at 137° (A. **228**, 353). Compare phenyl hydrazido-acetic acid. **Pyrazolon,** , is the lactazam, which may be derived from the unknown half-aldehyde of malonic acid (see oxymethylene acetic acid, p. 361).

9. KETONIC ACIDS.

These contain both the groups CO and CO_2H; they, therefore, show acid and ketone characters with all the specific properties peculiar to these. In conformity with the manner of designating the mono-substituted fatty acids and the various diketones (pp. 274 and 321), we distinguish the groups α-, β- and γ- of the ketonic acids:

$\overset{\beta}{C}H_3 . \overset{\alpha}{C}O . CO_2H$	$\overset{\gamma}{C}H_3 . \overset{\beta}{C}O . \overset{\alpha}{C}H_2 . CO_2H$	$\overset{\delta}{C}H_3 . \overset{\gamma}{C}O . \overset{\beta}{C}H_2 . \overset{\alpha}{C}H_2 . CO_2H$
α-Ketonic Acid	β-Ketonic Acid	γ-Ketonic Acid
Pyroracemic Acid	Acetoacetic Acid	Lævulinic Acid.

The α- and γ-acids are quite stable, even in a free condition. This is only the case with the β-acids when in the form of esters. If they are set free from these they readily decompose.

The names of the ketonic acids are usually derived from the fatty acids, inasmuch as the acid radicals are introduced into these; *e. g.*,—

$CH_3 . CO . CO_2H$	$CH_3 . CO . CH_2 . CO_2H$	$CH_3CO . \overset{\beta}{C}H_2 . \overset{\alpha}{C}H_2 . CO_2H$
Acetyl-formic Acid	Acetyl- or Aceto-acetic Acid	β-Acetyl-propionic Acid.

or these acids should be viewed as *keto*-substitution products of the fatty acids or oxofatty acids (p. 211):

$CH_3 . CO . CO_2H$	$CH_3 . CO . CH_2 . CO_2H$	$CH_3 . CO . CH_2 . CH_2 . CO_2H$
α-Ketopropionic Acid	β-Ketobutyric Acid	γ-Ketovaleric Acid
α-Oxopropionic Acid	β-Oxobutyric Acid	γ-Oxovaleric Acid.

The "Geneva names" are formed by the addition of the word "acid" to the names of the ketones, as the ketonic acids may be considered as the oxidation products of the latter:

CH_3COCO_2H	$CH_3CO . CH_2CO_2H$	$CH_3COCH_2CH_2CO_2H$
[Propanon Acid]	[2-Butanon Acid]	[3-Pentanon Acid].

Formation.—The more stable α-, γ- and δ-ketonic acids can be prepared by the oxidation of the secondary alcohol acids corresponding to them. Other methods will be given under the individual classes of these acids.

Transformations.—The ketone nature of these acids manifests itself in numerous reactions, *e. g.*, nascent hydrogen converts all the ketonic acids into the corresponding alcohol acids. They unite with alkaline sulphites, with hydroxylamine, and with phenylhydrazine.

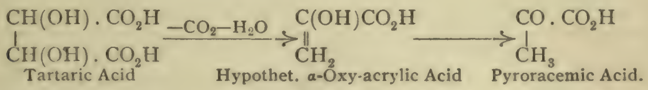
A. PARAFFIN KETONE CARBOXYLIC ACIDS.

α-Ketonic Acids—R . CO . CO_2H.

In this class the ketone group CO is in direct union with the acid-forming carboxyl group, CO_2H. We can view them as compounds of acid radicals with carboxyl, or as derivatives of formic acid, HCO . OH, in which the hydrogen linked to carbon is replaced by an acid radical. This view indicates, too, the general synthetic method of formation of these acids from the cyanides of acid radicals (p. 370), which, by the action of concentrated hydrochloric acid, are changed to the corresponding ketonic acids:

$$CH_3 . CO . CN + 2H_2O + HCl = CH_3 . CO . CO_2H + NH_4Cl.$$

(1) **Pyroracemic Acid,** Pyruvic Acid (acetyl formic acid), [*Propanon Acid*], $CH_3 . CO . CO_2H$, melting at +3° and boiling at 61° (12 mm.), was first obtained in the distillation of tartaric acid, racemic acid (Berzelius, 1835) and glyceric acid. (1) The acid is made by the distillation of tartaric acid alone (A. **172**, 142) or with potassium bisulphate (B. **14**, 321). We may assume that in this decomposition the first product is *a*-oxyacrylic acid, which at once rearranges itself into pyroracemic acid:



$$\underset{\text{Tartaric Acid}}{\begin{array}{l}CH(OH) . CO_2H\\ |\\ CH(OH) . CO_2H\end{array}} \xrightarrow{-CO_2-H_2O} \underset{\text{Hypothet. }\alpha\text{-Oxy-acrylic Acid}}{\begin{array}{l}C(OH)CO_2H\\ \|\\ CH_2\end{array}} \xrightarrow{\qquad} \underset{\text{Pyroracemic Acid.}}{\begin{array}{l}CO . CO_2H\\ |\\ CH_3\end{array}}$$

It is synthetically prepared from (2) *a*-dichlorpropionic acid (p. 275), when heated with water; (3) in the oxidation of *a*-oxypropionic acid or ordinary lactic acid with potassium permanganate; (4) by the decomposition of oxalacetic ester; (5) from acetyl cyanide by the action of hydrochloric acid (see above).

Pyroracemic acid is a liquid, soluble in alcohol, water and ether, and has an odor quite similar to that of acetic acid. It boils at 165–170°, decomposing partially into CO_2 and pyrotartaric acid ($2C_3H_4O_3 = C_5H_8O_4 + CO_2$). This change is more readily effected if the acid be heated to 100° with hydrochloric acid. It volatilizes without decomposition under reduced pressure. Its *ethyl ester* boils at 144° (B. **26**, R. 769, 775).

Transformations.—The acid reduces ammoniacal silver solutions with the production of a silver mirror, the decomposition products being CO_2 and acetic acid. When heated with dilute sulphuric acid to 150° it splits up into CO_2 and aldehyde, $CH_3 . COH$. This ready separation of aldehyde accounts for the ease with which pyroracemic acid enters into various condensations, *e.g.*, the formation of crotonic acid by the action of acetic anhydride (p. 278), and the condensations with dimethyl aniline and phenols in the presence of $ZnCl_2$. The acid condenses with the benzene hydrocarbons, in the presence of sulphuric acid, without decomposition (B. **14**, 1595; **16**, 2071; B. **18**, 987, and **19**, 1089).

Pyruvic acid is monobasic. Its salts crystallize with difficulty. Its zinc salt, $(C_3H_3O_3)_2Zn + 3H_2O$, is a crystalline powder, soluble with difficulty in water. All the salts are colored red by ferric chloride.

When the acid or its salts are heated with water, or if the acid be set free from its salts by mineral acids, it passes into a syrup-like, non-volatile mass.

Pyruvic acid forms crystalline compounds with the acid alkaline sulphites. It resembles the ketones in this respect. Nascent hydrogen (Zn and HCl, or HI) changes it to ordinary *a*-lactic acid, $CH_3 . CH(OH) . CO_2H$, and dimethyl racemic acid. Mercaptans—*e. g.*, phenyl-mercaptan, combine with pyroracemic acid to form

$CH_3C(OH)(SC_6H_5)CO_2H$ (B. **28**, 263). For the behavior of pyroracemic acid with NH_3, NH_2OH, $C_6H_5NH . NH_2$, consult "Nitrogen derivatives of the α-ketonic acids." It combines with CNH to form the nitrile of α-oxyisosuccinic acid. The change of pyroracemic acid on boiling with baryta water into *uvitic acid*, C_6H_3-[1. 3. 5]$(CH_3)(CO_2H)_2$, and *uvic acid* or *pyrotritartaric acid*, is most interesting. The uvitic acid formation is due to a condensation of pyroracemic acid with acetaldehyde. This is a reaction capable of wider generalization. For the condensation of the acid with formaldehyde consult tetramethylene dioxalic acid.

Halogen Substitution Products of Pyroracemic Acid.—*Trichlorpyroracemic Acid*, Isotrichlor-glyceric Acid, $CCl_3 . CO . CO_2H + H_2O = CCl_3 . C(OH)_2COOH$, melting at 102°, is produced (1) when $KClO_3$ and HCl act upon gallic acid and salicylic acid; (2) by the action of chlorine water upon chlorfumaric acid (B. **26**, 656); (3) from trichlor-acetyl cyanide.

Substitution products result by heating the acid with bromine and water to 100°; *dibrom-pyruvic acid*, $CBr_2H . C(OH)_2CO_2H + H_2O$, melts at 89°, anhydrous. *Tribrom-pyruvic acid*, $CBr_3 . C(OH)_2 . CO_2H + H_2O$, fuses at 90°, anhydrous. When heated with water or ammonia, it breaks up into bromoform, $CHBr_3$, and oxalic acid.

Homologues of Pyroracemic Acid.

Propionyl-carboxylic Acid, $C_2H_5 , CO . CO_2H$, boils at 74–78° (25 mm.).

Butyryl-carboxylic Acid, $C_3H_7 . CO . CO_2H$, boils at 185° (82–84 mm.).

Trimethyl-pyroracemic Acid, $(CH_3)_3 . C . CO . CO_2H$, results from the oxidation of pinacoline with potassium permanganate. It melts at 90° and boils at 185° (B. **23**, R. 21).

Nitrogen Derivatives of the α-Ketonic Acids.

(1). *α-Ketone amides* are produced by the action of cold concentrated hydrochloric acid upon the α-ketone nitriles. *Pyroracemamide*, $CH_3 . CO . CO . NH_2$, melts at 124°. *Propionyl Formamide*, $C_2H_5CO . CO . NH_2$, melts at 116° (B. **13**, 2121).

(2) *α-Ketone Nitriles* result on heating acid chlorides or bromides with silver cyanide:

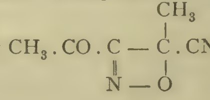
$$C_2H_3OCl + AgCN = C_2H_3O . CN + AgCl;$$

and when the aldoximes of the α-aldehyde ketones are treated with dehydrating agents, such as acetic anhydride (p. 326; B. **20**, 2196):

$$CH_3 . CO . CH : NOH = CH_3 . CO . CN + H_2O.$$

The acid cyanides are not very stable, and, unlike the alkyl cyanides, are converted by water or alkalies into their corresponding acids and hydrogen cyanide, $CH_3 . CO . CN + H_2O = CH_3 . CO . OH + CNH$. With concentrated hydrochloric acid, on the contrary, they sustain a transposition similar to that of the alkyl cyanides (p. 266), *i. e.*, carboxyl derivatives of the acid radicals—the so-called α-ketonic acids (see these)—are produced. Water is absorbed, and the amides of the α-ketonic acids are intermediate products (Claisen):

$$CH_3 . CO . CN \xrightarrow{H_2O} CH_3 . CO . CONH_2 \xrightarrow[HCl]{H_2O} CH_3COCOOH + NH_4Cl.$$

Acetyl Cyanide, $CH_3 . CO . CN$, boils at 93°. When preserved for some time, or by the action of KOH or sodium, it is transformed into a polymeric, crystalline compound, $(C_2H_3OCN)_2$, diacetyl cyanide, probably  $\begin{array}{ccccc} & & & CH_3 & \\ & & & | & \\ CH_3 . CO . & C & — & C & . CN \\ & \| & & | & \\ & N & — & O & \end{array}$ (B. **26**, R. 780). This melts at 69° and boils at 208°.

Diacetyl cyanide is also produced by the action of potassium cyanide upon acetic anhydride (B. **18**, 256). See Isomalic Acid.

Propionyl Cyanide, $CH_3 . CH_2 . CO . CN$, boils at 108–110°. **Dipropionyl Cyanide,** $(C_3H_5O . CN)_2$, melts at 59°, and boils at 200–210° (B. **18**, R. 140). **Butyryl Cyanide,** $C_3H_7 . CO . CN$, boils at 133–137°; **isobutyryl cyanide,** $C_3H_7 . CO . CN$, at 118–120°. These polymerize readily to dicyanides, which pass into alkyltartronic acids on treatment with hydrochloric acid.

(3) *Ethylimidopyruvyl chloride*, $CH_3CO . CCl : N . C_2H_5$, is a yellowish oil produced by the union of chloracetyl with ethylisocyanide (A. **280**, 298).

(4) *Chlorisonitrosoacetone*, $CH_3COC(NOH)Cl$, melting at 105°, is formed:

(1) By the action of nitric acid upon chloracetone;

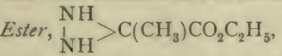
(2) By the action of chlorine upon isonitrosoacetone;

(3) When hydrochloric acid acts upon acetyl-methyl nitrolic acid, $CH_3 . CO . C(=NOH)ONO$ or $CH_3 . CO . C(=NOH)NO_2$—the product resulting from the action of nitric acid upon acetone (A. **277**, 318). The *oxime*, $CH_3 . C : NOH . C(: NOH)O . NO$, of this acid melts at 97° with decomposition.

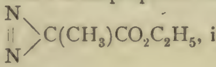
(5) *Imidopyroracemic Acid*, $CH_3C(NH)CO_2H$, is formed when ammonia acts upon pyroracemic acid, and when it decomposes a picoline dicarboxylic acid results—*uvitonic acid;* by the action of aniline the products are *Anilpyruvic Acid*, $CH_3 . C(: N . C_6H_5)CO_2H$, which fuses at 126° with decomposition (B. **27**, R. 508) and a quinoline carboxylic acid, *aniluvitonic acid.*

(6) *a-Oximido-fatty Acids*, or oximes of the *a*-ketonic acids, result (1) by the action of hydroxylamine upon *a*-ketonic acids, and (2) when nitrous acid acts upon monoalkyl acetoacetic esters (B. **15**, 1527). In the latter case the acetyl-group is displaced (B. **11**, 693). Acetic anhydride changes these acids to acid nitriles; carbon dioxide being eliminated.

a-Oximido-propionic Acid, Isonitroso-propionic Acid, $CH_3 . C = N(OH) . CO_2H$, decomposes at 177°. *a-Oximido-propionic Ethyl Ester*, $CH_3C = N(OH)CO_2C_2H_5$, melts at 94° and boils at 238° (B. **27**, R. 470). *a-Oximido-propionamide*, $CH_3 . C : N(OH)CONH_2$, melts at 174° (B. **28**, R. 766). *a-Oximido-propion-acetic Acid*, $CH_3C : N(O . CH_2CO_2H)CO_2H$, melts at 131° (B. **29**, R. 169). *a-Oximido-butyric Acid*, $CH_3 . CH_2C = (NOH)CO_2H$, and other *a*-oximido-acids are known. *a-Oximido-dibrom-pyroracemic Acid* has been obtained in two modifications (B. **25**, 904).



(7) *Hydrazipropionic Ethyl Ester*, $\left.\begin{matrix}NH\\ \mid\\ NH\end{matrix}\right>C(CH_3)CO_2C_2H_5$, melting at 115–117° (J. pr. Ch. [2] **44**, 554), results from pyroracemic acid and hydrazine. Mercuric oxide converts its methyl ester into *a*-diazopropionic methyl ester.



(8) *a-Diazopropionic Ester*, $\left.\begin{matrix}N\\ \|\\ N\end{matrix}\right>C(CH_3)CO_2C_2H_5$, is a yellow oil, obtained from the hydrochloride of alanine ethyl ester.

(9) *Phenylhydrazone-pyroracemic Acid*, $CH_3C(N = NHC_6H_5)CO_2H$, melts with decomposition about 192°, and is not only formed by the action of phenylhydrazine upon pyroracemic acid (B. **21**, 984), but also in the saponification of the reaction-product from diazobenzene chloride and methyl acetoacetic ester (B. **20**, 2942, 3398; **21**, 15; A. **278**, 285).

(10) *a-Amidothiolactic Acid*, $CH_3C(SH)(NH_2) . CO_2H$ (see p. 347).

β-Ketonic Acids.

In the β-ketonic acids the ketone oxygen atom is attached to the second carbon atom, counting from the carboxyl group forward. These compounds are very unstable when free and when in the form of salts. Heat decomposes them into carbon dioxide and ketones. Their esters, on the other hand, are very stable, can be distilled without decomposition, and serve for various and innumerable syntheses.

The β-, γ-, and δ-ketonic acids can also be considered as ketones in which an hydrogen atom has been replaced by carboxyl. In the

β-acids, which lose CO_2 readily, the carbonyl (CO) group and the CO_2H group are attached to the same carbon atom (compare malonic acid).

Acetoacetic Acid, Acetone-monocarboxylic Acid, $CH_3.CO.CH_2.CO_2H$, β-Ketobutyric Acid [Butanon Acid]. To obtain the acid, the esters are saponified *in the cold* by dilute potash, or the barium salt is decomposed with sulphuric acid, and the solution shaken with ether (B. **15**, 1781; **16**, 830). Concentrated over sulphuric acid, acetoacetic acid is a thick liquid, strongly acid, and miscible with water. When heated, it yields carbon dioxide and acetone:

$$CH_3.CO.CH_2.CO_2H = CH_3.CO.CH_3 + CO_2.$$

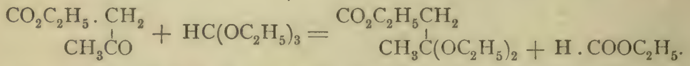
Nitrous acid converts it at once into CO_2 and isonitroso-acetone (p. 326). Its salts are not very stable. It is difficult to obtain them pure, and they sustain changes similar to those of the acid. Ferric chloride imparts to them, and also to the esters, a violet-red coloration. Occasionally the sodium or calcium salt is found in urine (B. **16**, 2314).

The stable acetoacetic esters, $CH_3.CO.CH_2.CO_2R$, are produced by the action of metallic sodium upon acetic esters. In this reaction the sodium compounds constitute the first product. The free esters result upon treating their sodium compounds with acids, *e. g.*, acetic acid. They are obtained pure by distillation. The acetoacetic esters are liquids, dissolving with difficulty in water. They possess an ethereal odor. They can be distilled without decomposition.

The esters of acetoacetic acid, contrary to expectation, possess an *acid-like* character. They dissolve in alkalies, forming salt-like compounds in which an hydrogen atom is replaced by metals.

Constitution.—Many reactions of acetoacetic ester are more simply explained by granting that it or its sodium compound has the constitution of β oxycrotonic ester, $CH_3.C(OH):CH.CO_2C_2H_5$ and $CH_3C(ONa) = CHCO_2C_2H_5$. However, in studying the oxymethylene bodies we learned to know derivatives possessing the atomic arrangement—C(OH) : CH—as represented in the β-oxycrotonic ester formula and were then convinced that their deportment was much different from that shown by acetoacetic ester.

The physical properties of the ester, its refraction (p. 65), its molecular rotation and its behavior toward the electric waves (p. 69) have also been determined, and it has been found that they harmonize with the ketone formula, $CH_3.CO.CH_2.CO_2C_2H_5$, alone (compare, however, B. **29**, 1723). The conduct of acetoacetic ester toward orthoformic ether is strong proof of its ketone nature. It reacts like the ketones with it, forming β-diethoxybutyric ester and formic ester (Claisen, B. **29**, 1006):



$$\begin{matrix} CO_2C_2H_5.CH_2 \\ \vert \\ CH_3CO \end{matrix} + HC(OC_2H_5)_3 = \begin{matrix} CO_2C_2H_5CH_2 \\ \vert \\ CH_3C(OC_2H_5)_2 \end{matrix} + H.COOC_2H_5.$$

However, the question whether the sodium salt does not probably have the formula $CH_3.C(ONa):CH.CO_2C_2H_5$ instead of $CH_3.CO.CHNa.CO_2.C_2H_5$, is at present still unanswered (A. **277**, 162).

Historical.—In 1863 Geuther investigated the action of sodium upon acetic ester. Simultaneously and quite independently of Geuther, Frankland and Duppa, in concluding their studies upon the action of zinc and alkyl iodides upon oxalic ether (p. 331), investigated the action of sodium and alkyl iodides upon acetic ester. J. Wislicenus has contributed very materially to the explanation of the reactions here involved (1877), A. **186**, 161.

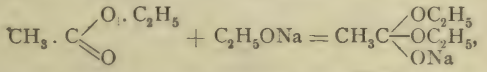
As the β-ketonic acids are so very unstable, their more stable esters are employed in their study. These can be made according to the following reactions:

Formation of Acetoacetic Ester and its Homologues.

(1) By the action of sodium or sodium alcoholate upon acetic ester. These reagents act similarly upon propionic ester, with the formation of α-propionyl propionic ester, $CH_3 . CH_2 . CO . CH(CH_3) . CO_2 . C_2H_5$.

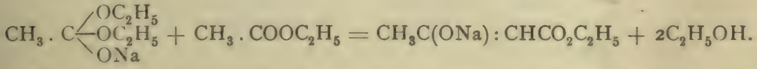
However, when sodium acts upon normal butyric ester, isobutyric ester and isovaleric ester, it is not the analogous bodies which result, but oxyalkyl derivatives of higher fatty acids (B. **22**, R. 22).

The formation of acetoacetic ester from acetic ester is due to the elimination of alcohol from two molecules of acetic ester by the action of sodium ethylate. Claisen considers that the addition of sodium ethylate to a molecule of acetic ester precedes the splitting-off of alcohol. A derivative of ortho-acetic acid is formed at first (p. 224):



$$CH_3 . C\begin{array}{l}\diagup O . C_2H_5\\ \diagdown O\end{array} + C_2H_5ONa = CH_3C\begin{array}{l}\diagup OC_2H_5\\ -OC_2H_5,\\ \diagdown ONa\end{array}$$

which rearranges itself with a second molecule of acetic ester to sodium acetoacetic ester and alcohol:

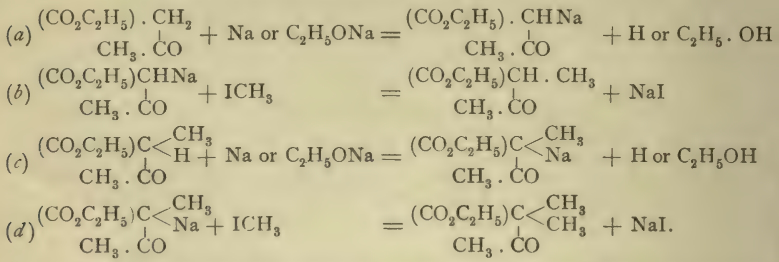


$$CH_3 . C\begin{array}{l}\diagup OC_2H_5\\ -OC_2H_5\\ \diagdown ONa\end{array} + CH_3 . COOC_2H_5 = CH_3C(ONa) : CHCO_2C_2H_5 + 2C_2H_5OH.$$

This view is based on the following facts: (1) The condensation of the two molecules of acetic ester can be effected, if less completely, by sodium ethylate (instead of sodium). (2) It has been shown in regard to certain acid esters, *e.g.*, benzoic ethyl ester, that they really combine with sodium ethylate to yield ortho-derivatives of the kind mentioned. (3) In other condensations, manifestly analogous to the ester formation, *e.g.*, the action of formic ester upon acid esters or ketones, the reaction proceeds very certainly to a marked degree in the direction indicated, with the formation of sodium oxyl-compounds, *e.g.*, $CO_2 . C_2H_5 . CH : CHONa$. (4) In the action of sodium upon isobutyric ester, in which the scheme of Claisen is no longer possible, a very different transposition actually takes place.

(2) The transposition of the sodium derivatives of the acetoacetic esters and mono-alkylic acetic esters with alkylogens, especially alkyl iodides and bromides.

(*a*) In acetoacetic ester only one hydrogen atom of the group CH_2 is replaceable by sodium. (*b*) By double decomposition through the agency of alkyl bromide or iodide, *one* alkyl group can be introduced for this sodium atom. (*c*) In these mono-alkylic acetoacetic esters the second hydrogen atom of the methylene group of acetoacetic ester can be replaced by sodium. The products are the sodium compounds of the mono-alkylic acetoacetic esters. (*d*) If alkyl iodides or bromides be again permitted to act upon these last derivatives, a second alkyl group may be introduced, yielding dialkylic acetoacetic esters, containing like or unlike alcohol radicals. The following equations represent the reactions just discussed. By means of them very many β-ketonic acid esters have been prepared:



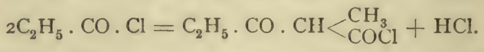
$$(a)\ \begin{array}{r}(CO_2C_2H_5).CH_2\\ |\ \ \ \\ CH_3.CO\end{array} + \text{Na or } C_2H_5ONa = \begin{array}{r}(CO_2C_2H_5).CHNa\\ |\ \ \ \ \ \ \ \ \\ CH_3.CO\ \ \ \ \ \end{array} + \text{H or } C_2H_5.OH$$

$$(b)\ \begin{array}{r}(CO_2C_2H_5)CHNa\\ |\ \ \ \ \ \ \ \ \\ CH_3.CO\ \ \ \ \ \end{array} + ICH_3 = \begin{array}{r}(CO_2C_2H_5)CH.CH_3\\ |\ \ \ \ \ \ \ \ \ \ \\ CH_3.CO\ \ \ \ \ \ \ \end{array} + NaI$$

$$(c)\ \begin{array}{l}(CO_2C_2H_5)C<\begin{array}{l}CH_3\\ H\end{array}\\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ |\\ \ \ \ \ \ \ \ \ CH_3.CO\end{array} + \text{Na or } C_2H_5ONa = \begin{array}{l}(CO_2C_2H_5)C<\begin{array}{l}CH_3\\ Na\end{array}\\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ |\\ \ \ \ \ \ \ \ \ CH_3.CO\end{array} + \text{H or } C_2H_5OH$$

$$(d)\ \begin{array}{l}(CO_2C_2H_5)C<\begin{array}{l}CH_3\\ Na\end{array}\\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ |\\ \ \ \ \ \ \ \ \ CH_3.CO\end{array} + ICH_3 = \begin{array}{l}(CO_2C_2H_5)C<\begin{array}{l}CH_3\\ CH_3\end{array}\\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ |\\ \ \ \ \ \ \ \ \ CH_3.CO\end{array} + NaI.$$

(3) A universal method, answering for the synthesis of the esters of the higher β-ketonic acids, consists in allowing ferric chloride to act upon the chlorides of the fatty acids. The first products in this instance are ketonic chlorides:



$$2C_2H_5.CO.Cl = C_2H_5.CO.CH<\begin{array}{l}CH_3\\ COCl\end{array} + HCl.$$

These chlorides, on treatment with water, split off CO_2 and become ketones (p. 209). If alcohols be employed, the products are *ketonic esters* (Hamonet, B. **22**, R. 766).

This method also permits of the preparation of β-ketonic esters from the higher fatty acid chlorides, *e. g.*, butyryl chloride, œnanthylic chloride:

$$C_2H_5.CO.CH<\begin{array}{l}CH_3\\ COCl\end{array} + C_2H_5OH = C_2H_5.CO.CH<\begin{array}{l}CH_3\\ CO_2C_2H_5\end{array} + HCl$$

α-Propionyl-propionic Ester.

Preparation of Acetoacetic Ester and the Alkyl Acetoacetic Esters.—Sixty parts of metallic sodium are gradually dissolved in 2000 parts of pure ethyl acetic ester. The excess of the latter is distilled off. On cooling, the mass solidifies to a mixture of sodium acetoacetic ester and sodium ethylate. The mass remaining liquid is mixed with acetic acid (50 per cent.) in slight excess. The oil separated and floating on the surface of the water is siphoned off, dehydrated with calcium chloride, and fractionated (A. **186**, 214, and **213**, 137). For the preparation of the dry sodium compound, see A. **201**, 143.

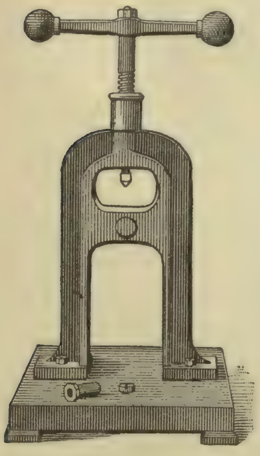


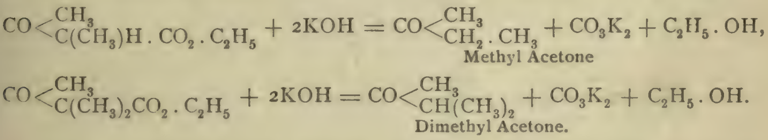
FIG. 10.

For the preparation of the alkyl acetoacetic esters according to the second method, it is not necessary to prepare pure sodium compounds. To the acetoacetic ester dissolved in 10 times its volume of absolute alcohol, add an equivalent amount of sodium and then the alkyl iodide, after which heat is applied. To introduce a second alkyl, employ again an equivalent quantity of the sodium alcoholate and the alkyl iodide (A. **186**, 220; **192**, 153). In some cases sodium hydroxide may be substituted for sodium ethylate in these syntheses (A. **250**, 123).

Or, sodium is allowed to act upon the sodium acetoacetic ester dissolved in some indifferent solvent, *e. g.*, ether, benzene, toluene, xylene. To get the sodium in a finely divided form, so that it may act with a perfectly untarnished surface, it is forced by a sodium press (Fig. 10) into the diluent or solvent. The greater or less firmness with which the halogen atom to be replaced is attached, determines the choice of the indifferent solvent. In many of these transpositions it has been found necessary to allow the sodium derivative of the respective β-ketonic ester to act for days upon the halogen substitution product at the boiling temperature of the solvent (compare A. 259, 181).

Transpositions of the β-Ketonic Esters.

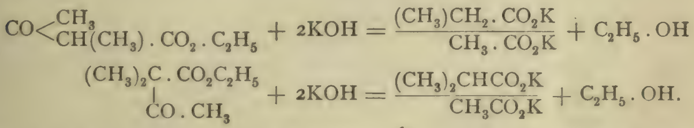
(1*a*) On heating the mono- or dialkylic acetoacetic esters with alkalies in *dilute* aqueous or alcoholic solution, or with barium hydroxide, they decompose after the manner of acetoacetic esters (p. 371), forming ketones (alkylic acetones) (*ketone decomposition*):



$$CO\begin{matrix}\diagup CH_3 \\ \diagdown C(CH_3)H.CO_2.C_2H_5\end{matrix} + 2KOH = \underset{\text{Methyl Acetone}}{CO\begin{matrix}\diagup CH_3 \\ \diagdown CH_2.CH_3\end{matrix}} + CO_3K_2 + C_2H_5.OH,$$

$$CO\begin{matrix}\diagup CH_3 \\ \diagdown C(CH_3)_2CO_2.C_2H_5\end{matrix} + 2KOH = \underset{\text{Dimethyl Acetone.}}{CO\begin{matrix}\diagup CH_3 \\ \diagdown CH(CH_3)_2\end{matrix}} + CO_3K_2 + C_2H_5.OH.$$

(1*b*) At the same time another splitting-off takes place, by which the alkylic acetic acids, *i. e.*, the higher fatty acids are produced along with acetic acid (*acid decomposition*):



$$CO\begin{matrix}\diagup CH_3 \\ \diagdown CH(CH_3).CO_2.C_2H_5\end{matrix} + 2KOH = \frac{(CH_3)CH_2.CO_2K}{CH_3.CO_2K} + C_2H_5.OH$$

$$\begin{matrix}(CH_3)_2C.CO_2C_2H_5 \\ | \\ CO.CH_3\end{matrix} + 2KOH = \frac{(CH_3)_2CHCO_2K}{CH_3CO_2K} + C_2H_5.OH.$$

Both of these reactions, in which decomposition occurs (the splitting-off of ketone and of acid), usually take place simultaneously. In using dilute potash or caustic baryta, the ketone-decomposition predominates, whereas, with very concentrated alcoholic potash, the same may be asserted in regard to the acid-decomposition (J. Wislicenus, A. 190, 276). The splitting-off of ketone, with elimination of CO_2, occurs almost exclusively on boiling with sulphuric or hydrochloric acid (1 part acid and 2 parts water).

This breaking-down of the mono- and di-alkyl acetoacetic esters is the basis of the application of these bodies in the production of mono- and dialkylic acetones (p. 210), as well as mono- and dialkylic acetic acids.

(2) The acetoacetic esters are changed by nascent hydrogen (sodium amalgam) into the corresponding β-oxy-acids (p. 330):

$$CH_3.CO.CH_2.CO_2.C_2H_5 + H_2 + H_2O = CH_3.CH(OH).CH_2.CO_2H + C_2H_5.OH.$$

They are saponified at the same time.

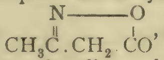
(3) Chlorine and bromine produce halogen substitution products of the acetoacetic esters.

(4) PCl_5 replaces the oxygen of the β-CO group by 2 atoms of chlorine. The *chloride*, $CH_3.CCl_2.CH_2.CO.Cl$, readily splits off hydrochloric acid and yields two chlor-crotonic acids (p. 282).

(5) Orthoformic ester replaces the oxygen of the β-CO group by two ethoxy-groups. The product is β-diethylbutyric ester which readily splits off alcohol and yields β-ethoxycrotonic ester (see 10, p. 376).

(6) Ammonia, aniline, hydrazine and phenylhydrazine, acting upon acetoacetic ester, produce β-amido-, β-anilido-, β-hydrazido-, and β-phenylhydrazidocrotonic acid (p. 363), substances which easily condense. They yield semicarbazone (A. **283**, 29) with semicarbazide.

(7) All the acetoacetic esters combine with hydroxylamine to form esters of the corresponding β-isonitroso fatty acids. When these are set free from their salts they split off water and pass into anhydrides (p. 327): *β-Oximido-butyric anhydride*, methyl-isoxazolon, , melting at 169–170° (B. **28**, 2731).



(8) Nitric oxide and sodium ethylate change sodium acetoacetic ester into the disodium derivative of isonitramine acetoacetic ester (B. **28**, 2297):

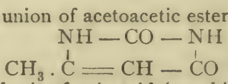
$$\begin{matrix}CO_2C_2H_5\\CH_3CO\end{matrix}\!>CHNa + 2NO + C_2H_5ONa = \begin{matrix}CO_2C_2H_5\\CH_3.CO\end{matrix}\!>C<\!\begin{matrix}N_2O_2Na\\Na\end{matrix} + C_2H_5.OH.$$

(9) Nitrous acid changes them to the isonitroso-derivatives, $CH_3.CO.C(N.OH).CO_2R$, which readily break up into isonitroso-acetone, CO_2 and alcohols (see below). Nitrous acid, acting upon mono-alkylic acetoacetic esters, displaces the acetyl group and leads to the formation of α-isonitroso-fatty acids (p. 371), whereas the free monoalkylic acetoacetic esters, under like treatment, split off CO_2 and yield isonitroso-ketones (p. 282).

(10) Diazomethane converts acetoacetic ester into β-methoxy-cis-crotonic ester (p. 363) (B. **28**, 1626).

(11) Benzene diazosalts act like nitrous acid upon acetoacetic ester (B. **21**, 549; A. **247**, 217).

(12) An important reaction is the union of acetoacetic ester with urea, when water is eliminated and **Methyluracil**, , is formed. This is the starting-out substance for the synthesis of uric acid (see this).



(13) Amidines convert acetoacetic ester into pyrimidine compounds.

Nucleus-synthetic Reactions.

(1) Heated alone, acetoacetic ester is changed to dehydracetic acid (see this), the δ-lactone of an unsaturated δ-oxy-diketone carboxylic acid.

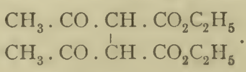
(2) The action of sulphuric acid causes acetoacetic ester to pass into a condensation product, iso-dehydracetic acid, the δ-lactone of an unsaturated δ-oxy-dicarboxylic acid.

(3) Prussic acid unites with acetoacetic ester, forming the nitrile of α-methyl malic ester.

The nucleus-synthetic reactions of sodium acetoacetic ester and copper acetoacetic ester are far more numerous.

(4) It has been repeatedly mentioned that the sodium acetoacetic esters could be applied in the building-up of the mono- and dialkylic acetoacetic esters, and also, therefore, in the preparation of mono- and dialkyl acetones, as well as mono- and dialkylic acetic acids.

(5) Iodine converts sodium acetoacetic ester into diaceto-succinic ester,



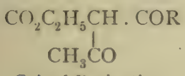
$$\begin{matrix}CH_3.CO.CH.CO_2C_2H_5\\ |\\ CH_3.CO.CH.CO_2C_2H_5\end{matrix}.$$

This body is also produced in the electrolysis of sodium acetoacetic ester (B. **28**, R. 452).

(6) Chloroform and sodium acetoacetic ester unite to oxyuvitic acid, $C_6H_2(CH_3)(OH)(CO_2H)_2$.

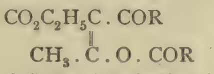
Furthermore, monochloracetone, chlorcyanogen, acid haloids, and monohalogen substitution products of mono- and dicarboxylic esters react with sodium acetoacetic ester. Copper acetoacetic ester is most advantageously used with phosgene (B. **19**, 19).

When acid chlorides act upon acetoacetic ester (this action has been most carefully studied with benzoyl chloride, Claisen, A. **291**, 65, 110), the first *acyl*, as a rule, attaches itself to the carbon, forming a *C-monacyl derivative*, while the second goes to the oxygen. The *O-monacyl derivatives* (the β-oxycrotonic acid compounds), isomeric with the C-monacyl derivatives can also be obtained from the acetoacetic esters with acid chlorides and pyridine (private communication from L. Claisen):



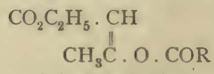
$$\begin{array}{c}CO_2C_2H_5CH\,.\,COR\\ |\\ CH_3CO\end{array}$$

C-Acyl Derivative



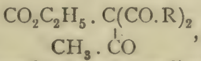
$$\begin{array}{c}CO_2C_2H_5C\,.\,COR\\ \|\\ CH_3\,.\,C\,.\,O\,.\,COR\end{array}$$

O,C-Diacyl Derivative



$$\begin{array}{c}CO_2C_2H_5\,.\,CH\\ \|\\ CH_3C\,.\,O\,.\,COR\end{array}$$

O-Acyl Derivative.

C *Diacyl Derivatives*,  $\begin{array}{c}CO_2C_2H_5\,.\,C(CO.R)_2\\ |\\ CH_3\,.\,CO\end{array}$, are not produced in the acylation of acetoacetic ester. Chlorcarbonic ester, ordinarily acting like the many related acid chlorides, forms an exception to the rule given in the preceding lines, for when it acts upon sodium acetoacetic ester it yields O-acyl derivatives almost exclusively.

For these reasons and for many others analogous to them, it is uncertain whether the C-sodium formula, $CH_3\,.\,CO\,.\,CHNa\,.\,CO_2C_2H_5$, or the O-sodium formula, $CH_3\,.\,C(ONa):CH\,.\,CO_2C_2H_5$, should be ascribed to sodium acetoacetic ester (compare p. 346).

(7) Aldehydes, *e. g.*, acetaldehyde, and acetoacetic ester unite to ethidene-mono- and ethidene bisacetoacetic esters. The latter γ-diketones especially are important, because by an intramolecular exit of water from CO and CH_3 they condense to ketohydrobenzene derivatives (A. **288**, 323), and with ammonia yield hydropyridine bodies.

(8) Acetoacetic ester condenses similarly with orthoformic ester to the ethoxymethylene derivative $(C_6H_8O_2):CHOC_2H_5$, on the one hand, and on the other to the methylene derivative $(C_6H_8O_3):CH\,.\,(C_6H_9O_3)$ (B. **26**, 2729).

(9) Resorcinol and acetoacetic ester condense to β-methylumbelliferone (B. **29**, 1794).

Ethyl Acetoacetic Ester, $CH_3\,.\,CO\,.\,CH_2\,.\,CO_2\,.\,C_2H_5 = C_6H_{10}O_3$, *Acetoacetic Ester*, boiling at 181° (760 mm.) and 72° (12 mm.), is a pleasantly smelling liquid, of sp. gr. 1.0256 at 20°. It distils over with steam. The ester is only slightly soluble in water. Ferric chloride colors it violet.

Boiling alkalies or acids convert the ester into acetone, carbon dioxide and alcohol. In addition to its formation by the action of sodium or sodium ethylate upon ethyl acetic ester, it results by the partial decomposition of acetone dicarbonic ester (see this), $CO_2C_2H_5CH_2COCH_2CO_2C_2H_5$.

The *sodium salt*, $CH_3COCHNaCO_2C_2H_5$ or $CH_3(CONa):CHCO_2C_2H_5$, crystallizes in long needles. The *copper salt*, $(C_6H_9O_3)_2Cu$, is produced when a copper acetate solution is mixed with an alcoholic solution of acetoacetic ester and a sufficient quantity of ammonia is added.

The following are some of the numerous β-ketonic esters: *Methyl Acetoacetic*

Ester, boiling at 169° (760 mm.). *Methyl Acetoacetic Methyl Ester*, $CH_3COCH(CH_3)CO_2CH_3$, boils at 177°; the *ethyl ester* at 187°; *Ethyl Acetoacetic Methyl Ester*, $CH_3.CO.CH(C_2H_5)CO_2CH_3$, boiling at 190°; *ethyl ester* at 198°. *Dimethyl Acetoacetic Ester*, $CH_3COC(CH_3)_2CO_2C_2H_5$, boils at 184°. *Diethyl Acetoacetic Ester* boils at 218°. n-*Propyl Acetoacetic Ester* boils at 208°. *Methyl Ethyl Acetoacetic Ester* boils at 198°. *Propionyl Propionic Ester*, *Methyl Propionyl Acetic Ester*, $CH_3CH_2COCH(CH_3).CO_2C_2H_5$, boils at 196°.

β-Diethoxybutyric Acid, $CH_3.C(O.C_2H_5)_2CH_2CO_2H$, is a syrupy liquid, which decomposes on the application of heat into CO_2 and acetone ortho-ethyl ether (p. 219). Its sodium salt is obtained by means of alcoholic sodium hydroxide from β-diethoxy-butyric ester, $CH_3.C(O.C_2H_5)_2CH_2CO_2C_2H_5$, the product of the transposition of acetoacetic ester and ortho-formic ester (B. **29**, 1006). β-Diethoxybutyric ester decomposes upon distillation into alcohol and β-ethoxycrotonic ester (p. 363). *β-Dithioethyl-butyric Ester*, $CH_3C(SC_2H_5)_2CH_2CO_2C_2H_5$, see B. **19**, 2810; **29**, 1648.

Derivatives of the β-Ketonic Acids, containing Nitrogen.

1. *Amides.* Ammonia converts acetoacetic esters into **β-Amidocrotonic Esters**, while the monomethyl- and monoethyl-acetoacetic ester, with the same reagent, yield the amides:

Methyl Acetoacetamide, $CH_3.CO.CH(CH_3)CO.NH_2$, melting at 73°; *Ethyl Acetoacetamide*, melting at 96° (A. **257**, 243).

2. *Cyanacetone*, Acetoacetic Nitrile, $CH_3.CO.CH_2.CN$, boiling at 120 to 125°, results from the interaction of chloracetone and potassium cyanide (B. **25**, 2679); from imidoacetonitrile and hydrochloric acid, and from α-methyl isoxazole (p. 327).

3. *Imidoacetoacetic Nitrile*, $CH_3.C(:NH)CH_2.CN$, melting at 52°, is produced by the polymerization of acetonitrile with metallic sodium (J. pr. Ch. [2] **52**, 81).

For the action of aniline, hydrazine, phenylhydrazine and semi-carbazide, hydroxylamine, nitrous acid, nitric oxide, diazomethane, benzene diazosalts, urea and amidines upon β-ketonic esters, compare the reactions 5–12, pp. 375, 376.

4. *Dinitrocaproic Acid*, α-Dimethyl-β-dinitrobutyric Acid, $CH_3.C(NO_2)_2.C(CH_3)_2CO_2H$, melts with decomposition at 215° C. It results from the prolonged boiling of camphor with nitric acid (B. **26**, 3051).

Halogen Substitution Products of the β-Ketonic Esters.

Chlorine alone or in the presence of sulphuryl chloride acting upon acetoacetic ester replaces the hydrogen atoms both of the CH_2 and CH_3 groups by chlorine. The hydrogen of the CH_2 group is first substituted, but in the case of bromine the substitution begins with the CH_3 group (A. **278**, 61).

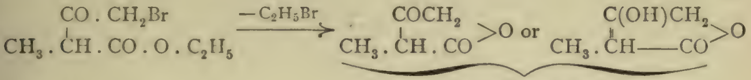
α-Chlor-acetoacetic Ester, $CH_3.CO.CHCl.CO_2.C_2H_5$, with a very penetrating odor, boils at 109° (10 mm.).

α-Brom-acetoacetic Ester, $CH_3.CO.CHBr.CO_2.C_2H_5$, boils at 90°–100° (20 mm.). It is formed when bromine acts upon copper acetoacetic ester. HBr gradually (B. **27**, 3168) changes it to γ-brom-acetoacetic ester, $CH_2Br.CO.CH_2.CO_2C_2H_5$, melting at 125° (8–10 mm.) (B. **29**, 1042).

The constitution of these two bodies has been established by condensing them with thiourea to the corresponding thiazole derivatives.

αα-Dichlor-acetoacetic Ester, $CH_3.CO.CCl_2.CO_2.C_2H_5$, is a pungent-smelling liquid, boiling at 205°. Heated with HCl it decomposes into α-dichloracetone, $CH_3.CO.CHCl_2$, alcohol and CO_2; with alkalies it yields acetic and dichloracetic acids. *αα-Dibrom-acetoacetic Ester* is a liquid. It yields a *dioxime*, $CH_3C(NOH)C(NOH)CO_2C_2H_5$, melting at 142°. *αγ-Dibrom-acetoacetic Ester*, $CH_2Br.CO.CHBr.CO_2C_2H_5$, melts at 45–49°.

Bromine converts the mono-alkylic acetoacetic esters into monobrom- and dibrom-derivatives. According to Demarçay (B. **13**, 1479, 1870) the monobrom-bodies, when heated alone or with water, split off ethyl bromide and yield peculiar acids; thus, brom-methyl acetoacetic ester gave *Tetrinic Acid* or *Methyl Tetronic Acid*, while bromethyl acetoacetic ester yielded *Pentinic Acid* or *Ethyltetronic Acid* (L. Wolff, A. **291**, 226):



$$\begin{array}{l} CO.CH_2Br \\ CH_3.\overset{|}{C}H.CO.O.C_2H_5 \end{array} \xrightarrow{-C_2H_5Br} \underbrace{\begin{array}{l} COCH_2 \\ CH_3.\overset{|}{C}H.CO \end{array}\!\!>O \text{ or } \begin{array}{l} C(OH)CH_2 \\ CH_3.\overset{\|}{C}H\text{---}CO \end{array}\!\!>O}_{\text{Tetrinic Acid = Methyl-tetronic Acid.}}$$

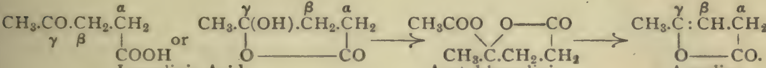
Tetrinic Acid = Methyl-tetronic Acid.

These acids will be discussed later as lactones of oxy-ketonic acids, together with the oxidation products of triacid alcohols.

The dibrom-derivatives treated with alcoholic potash yield oxy-tetrinic acid, oxy-pentinic acid, etc. Gorbow (B. **21**, R. 180) found them to be homologues of fumaric acid. Oxy-tetrinic acid is mesaconic acid (see this); while oxypentinic acid is ethyl fumaric acid (see this), etc.

γ-Ketonic Acids.

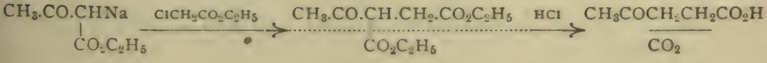
These acids are distinguished from the acids of the β-variety by the fact that when heated they do not yield CO_2, but split off water and pass into unsaturated γ-lactones. They form γ-oxyacids on reduction, which readily pass into saturated γ-lactones. An interesting fact in this connection is that they yield remarkably well crystallized acetyl derivatives when treated with acetic anhydride. This reaction, as well as the production of unsaturated γ-lactones, on distillation, argue for the view that the γ-ketonic acids are γ-oxylactones:



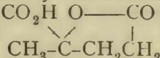
$$\begin{array}{l} CH_3.CO.CH_2.\overset{\alpha}{C}H_2 \\ \quad\ \gamma \quad \beta \quad\ \ \overset{|}{C}OOH \end{array} \text{ or } \begin{array}{l} CH_3.\overset{\gamma}{C}(OH).\overset{\beta}{C}H_2.\overset{\alpha}{C}H_2 \\ \qquad\ \ \overset{|}{O}\text{————}\overset{|}{C}O \end{array} \longrightarrow \begin{array}{l} CH_3COO \quad O\text{—}CO \\ \qquad\ \ \diagdown\diagup \qquad\ | \\ CH_3.C.CH_2.CH_2 \end{array} \longrightarrow \begin{array}{l} CH_3.\overset{\gamma}{C}:\overset{\beta}{C}H.\overset{\alpha}{C}H_2 \\ \qquad \overset{|}{O}\text{——}\overset{|}{C}O. \end{array}$$

Lævulinic Acid — Acetyl-lævulinic Acid — α-Angelica Lactone.

Lævulinic Acid, β-Aceto-propionic Acid, $C_5H_8O_3 = CH_3.CO.CH_2.CH_2.CO_2H$, or $CH_3.C(OH).CH_2.CH_2COO$, melts at 32.5°; boils at 144° (12 mm.), 239° at the ordinary pressure, when slight decomposition ensues. γ-Ketovaleric Acid, or γ-Oxovaleric Acid [4-Pentanon Acid] is isomeric with methyl acetoacetic acid, which may be designated α-aceto-propionic acid. Lævulinic acid can be obtained from the *hexoses* (see these) on boiling them with dilute hydrochloric or sulphuric acid. It is more easily obtained from lævulose—hence the name—than from dextrose. It is prepared on heating cane-sugar or starch with hydrochloric acid (B. **19**, 707, 2572; **20**, 1775; A. **227**, 99). Its constitution is evident from its indirect synthesis: sodium acetoacetic ester and chloracetic ester yield aceto-succinic ester, which, on boiling with hydrochloric acid or baryta water, loses CO_2 and passes into lævulinic acid (Conrad, A. **188**, 223):



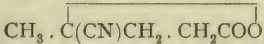
$$\begin{array}{l} CH_3.CO.CHNa \\ \qquad\quad\ \ \overset{|}{C}O_2C_2H_5 \end{array} \xrightarrow{ClCH_2CO_2C_2H_5} \begin{array}{c} CH_3.CO.CH.CH_2.CO_2C_2H_5 \\ CO_2C_2H_5 \end{array} \xrightarrow{HCl} \begin{array}{c} CH_3COCH_2CH_2CO_2H \\ \overline{CO_2} \end{array}$$

It is furthermore obtained by the action of concentrated H_2SO_4 upon methyl-glutolactonic acid,  $\begin{matrix} CO_2H & O\text{——}CO \\ \searrow\swarrow & | \\ CH_3\text{-}C\text{-}CH_2 & CH_2 \end{matrix}$; by the oxidation of its corresponding β-acetopropyl alcohol (p. 318), and by the oxidation of methyl heptenone (p. 221), of linalol and geraniol, two bodies belonging to the group of olefine terpenes.

Lævulinic acid dissolves very readily in water, alcohol and ether, and sustains the following transformations: (1) By slow distillation under the ordinary pressure it breaks down into water and α- and β-angelica lactones (p. 362). (2) When heated to 150–200° with hydriodic acid and phosphorus, lævulinic acid is changed to n-valeric acid. (3) By the action of sodium amalgam sodium γ-oxyvalerate is produced. The acid liberated from this becomes γ-valerolactone. (4) Dilute nitric acid converts lævulinic acid partly into acetic and malonic acid and partly into succinic acid and carbon dioxide.

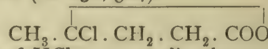
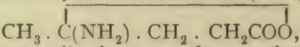
(5) Bromine converts the acid into substitution products, p. 381.

(6) Iodic acid changes it to *bi-iodo-acetacrylic acid.* (7) P_2S_3 converts it into *thiotolene*, $C_4H_3S.CH_3$. For the behavior of lævulinic acid with hydroxylamine and phenylhydrazine consult the paragraph relating to the nitrogen derivatives of the γ-ketonic acids.

Nucleus-synthetic Reactions: (8) Prussic acid and lævulinic acid yield the nitrile of lactonic acid:  $CH_3.\overline{C(CN)CH_2.CH_2COO}$, see methyl oxyglutaric acid. (9) Benzaldehyde and lævulinic acid condense in acid solution to *β-benzal-lævulinic acid*, and in alkaline solution to *δ-benzal-lævulinic acid* (A. **258**, 129; B. **26**, 349).

Lævulinic Acid Derivatives.—The *calcium salt*, $(C_5H_7O_3)_2Ca + 2H_2O$. The *silver salt*, $C_5H_7O_3Ag$, is a characteristic, crystalline precipitate, dissolving in water with difficulty. The *methyl ester*, $C_5H_7(CH_3)O_3$, boils at 191°, the *ethyl ester* at 200°.

Acetyl Lævulinic Acid, γ-Acetoxyl-γ-valerolactone,  $\begin{matrix} CH_3COO\searrow & \swarrow O.CO \\ CH_3.C.CH_2. & CH_2 \end{matrix}$, is particularly noteworthy. It melts at 78°, and is formed from lævulinic acid and acetic anhydride; from silver lævulinate and acetyl chloride; from lævulinic chloride and silver acetate, as well as from α-angelica lactone and acetic acid. The last method of formation, as well as the formation of α- and β-angelica lactone by acetolævulinic acid are most easily understood upon the assumption that the constitution is really as indicated in the formula shown above (A. **256**, 314).

Lævulinic Chloride, γ-Chlorvalerolactone,  $CH_3.\overline{CCl.CH_2.CH_2.COO}$, boiling at 80° (15 mm.), is produced by the addition of HCl to α-angelica lactone, and by the action of acetyl chloride upon lævulinic acid (A. **256**, 334). *Lævulinamide*, γ-Amidovalerolactone,  $CH_3.\overline{C(NH_2).CH_2.CH_2COO}$, has been obtained from lævulinic ester, and from α-angelica lactone and ammonia (A. **229**, 249).

Homologous Lævulinic Acids are obtained from the homologues of acetosuccinic ester:

β-Methyl-lævulinic Acid, β-Aceto-butyric Acid, $CH_3.CO.CH{<}{\begin{smallmatrix}CH_3\\CH_2.CO_2H\end{smallmatrix}}$, boils at 242° and melts at —12°.

α-Methyl-lævulinic Acid, β-Aceto-isobutyric Acid, $CH_3.CO.{\begin{smallmatrix}CH_2\\CH_3\end{smallmatrix}}{>}CH.CO_2H$, boils at 248°. *α-Ethyl Lævulinic Acid*, $CH_3CO.CH_2CH(C_2H_5).CO_2H$, boils at 250–252°.

Mesitonic Acid, *a*-Dimethyl lævulinic acid, $CH_3 . CO . CH_2C(CH_3)_2CO_2H$, melting at 74° and boiling at 138° (15 mm.), results when the addition product of hydrochloric acid and mesityl oxide is treated with potassium cyanide, and the nitrile then saponified with hydrochloric acid (A. **247,** 99), as well as by heating mesitylenic acid with hydrochloric acid (B. **25**, R. 905). Nitric acid oxidizes mesitonic acid to dimethyl malonic acid.

δ-Dimethyl Lævulinic Acid, $(CH_3)_2CH . CO . CH_2 . CH_2 . CO_2H$, melting at 40°, is produced when sodium malonic ester, from the transposition product of *γ*-brom-dimethyl acetoacetic ester, is heated with dilute sulphuric acid (B. **30**, 864).

Homolævulinic Acid, *δ*-methyl lævulinic acid, $CH_3 . CH_2 . CO . CH_2 . CH_2 . CO_2H$, melting at 32°, is obtained, together with an oxycaprolactone, from *βγ*-dibromcaproic acid (A. **268,** 69).

δ-Dimethyl Lævulinic Acid, $(CH_3)_2CH . CO . CH_2 . CH_2 . CO_2 H$, melting at 41°, is prepared by the action of a soda solution upon isoheptenic dibromide (p. 284) (A. **288,** 183).

Halogen *γ*-Ketonic Acids.—*a-Brom-lævulinic Acid*, $CH_3CO.CH_2.CHBr.CO_2H$, melting at 79°, is produced when HBr acts upon *β*-acetoacrylic acid. Boiling water converts it into *a*-hydroxy-lævulinic acid (see this).

***β*-Bromlævulinic Acid,** $CH_3 . CO . CHBr . CH_2 . CO_2H$, melts at 59°, and is produced in the bromination of lævulinic acid, as well as by the action of water upon the addition product of bromine and *a*-angelica lactone. Warming with sodium hydroxide converts the *β*-bromlævulinic acid into *a*-hydroxy-lævulinic acid and *β*-aceto-acrylic acid. Aniline converts brom-lævulinic acid into Py-2.3-dimethyl-indol (B. **21**, 3360), while ammonia changes it to tetramethylpyrazine.

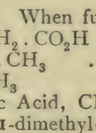
aβ-Dibrom-lævulinic Acid, $CH_3 . CO . CHBr . CHBr . CO_2H$, melting at 108°, is prepared from *β*-acetacrylic acid and Br_2. *βδ-Dibrom-lævulinic Acid*, $CH_2Br . CO . CHBr . CH_2 . CO_2H$, melting at 114–115°, is produced in the bromination of lævulinic acid. It yields diacetyl (p. 322) and glyoxyl propionic acid, $HOC . CO . CH_2 . CH_2 . CO_2H$, when it is boiled with water. Concentrated nitric acid converts it into dibrom-dinitromethane and monobrom-succinic acid, while with concentrated sulphuric acid it yields two isomeric dibrom-diketo-R-pentenes.

Nitrogen Derivatives of the *γ*-Ketonic Acids.

(1) *Lævulinamide*, $CH_3 . CO . CH_2 . CH_2 . CONH_2$ or $CH_3C(NH_2)CH_2 . CH_2 . COO$, melts at 107° (A. **229,** 260).

(2) *Action of Hydrazine*, $NH_2 . NH_2$: *Lævulinic Hydrazide*, $CH_3 . CO . CH_2 . CH_2 . CO . NH . NH_2$, melts at 82°. On the application of heat it passes into a lactazam (p. 363): 3-*Methyl pyridazolon*, 3-*Methyl pyridazinone*, $CH_3 . (C = N . NH)CH_2 . CH_2 . CO$, melts at 94° (B. **26,** 408; J. pr. Ch. [2] **50,** 522).

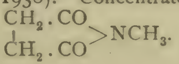
(3) *Action of Phenylhydrazine*, $NH_2 . NH . C_6H_5$: The first product is a hydrazone, which yields a lactazam when heated. *Lævulinic Phenylhydrazone*, $CH_3C(= N . NHC_6H_5)CH_2 . CH_2 . CO_2H$, melts at 108°. 3-*Methyl*-n-*phenyl pyridazolon*, $CH_3 . C(:N . NC_6H_5)CH_2 . CH_2CO$, melts at 81° (A. **253,** 44). When fused with zinc chloride it becomes dimethyl indol-acetic acid,



$$C_6H_4\left\langle\begin{matrix} C = CH_2 . CO_2H \\ \quad C . CH_3 \\ N - CH_3 \end{matrix}\right.$$

. *Phenylhydrazone-mesitonic Acid*, Phenylhydrazone-*a*-dimethyl lævulinic Acid, $CH_3C(N : NHC_6H_5)CH_2 . C(CH_3)_2CO_2H$, melts at 121.5°. 3-Methyl-1-dimethyl-n-phenyl pyridazolon, $CH_3C(:NNC_6H_5)CH_2C(CH_3)_2CO$, melts at 84° (A. **247,** 105).

(4) *Action of Hydroxylamine*: *Lævulinic Oxime*, $CH_3C(NOH)CH_2CH_2CO_2H$, melts at 95° (B. **25,** 1930). Concentrated sulphuric acid re-arranges this oxime into succinmethylimide,



$$\begin{matrix} CH_2 . CO \\ | \\ CH_2 . CO \end{matrix}\!\!>NCH_3.$$

δ-Ketonic Acids.

Such acids have been prepared from acetyl glutaric acids (see these) by the splitting-off of CO_2. On reduction they yield *δ-lactones* (p. 318).

γ-**Aceto-butyric Acid**, $CH_3 . CO . CH_2 . CH_2 . CH_2 . CO_2H$, melts at 13° and boils at 275°. Sodium amalgam converts it into a salt of δ-oxycaproic acid, which yields a δ-lactone (A. **216**, 127).

It is formed by the oxidation of γ-acetobutyl alcohol (p. 318) and dihydroresorcinol by baryta water. Sodium ethylate changes it back into dihydroresorcinol.

γ-Ethyl-γ-Acetyl Butyric Acid, $CH_3 . CO . CH(C_2H_5)CH_2 . CH_2 . CO_2H$, boils at 173° (10 mm.); at 280° (760 mm.). *Butyrobutyric Acid*, $CH_3 . CH_2 . CH_2 . CO . CH_2 . CH_2 . CH_2 . CO_2H$, from conine, melts at 34°.

Certain higher ketonic acids have been prepared by the oxidation of hydroaromatic compounds of the terpene group, and are important in determining the constitution of the latter. Other ketonic acids result from the hydrolysis of acetylene carboxylic acids by means of concentrated sulphuric acid. A case in point is 10-*Ketostearic Acid*, from stearolic acid (p. 287), which is produced on treating oleic and elaïdic dibromides with alcoholic potash. See oleic acid (p. 285) for the value of these ketonic acids in determining the constitution of the olefine and acetylene carbonic acids, which are closely related to them.

5-*Isopropyl heptan-2-on Acid*, β-isopropyl δ-acetyl valeric acid, $CH_3 . CO . CH_2 . CH_2CH(C_3H_7)CH_2CO_2H$, from tetrahydrocarvone, melts at 40° and boils at 192° (20 mm.). 2-6-*Dimethyl octan-3-on Acid*, β-methyl δ-isobutyl valeric acid, $CH_3 . CH(CH_3) . CO . CH_2 . CH_2CH(CH_3)CH_2CO_2H$, from menthone, boils at 186° (20 mm.). *Undecanonic Acid*, $CH_3 . CO(CH_2)_8CO_2H$ (?), from undecolic acid, melts at 49°.

10-*Ketostearic Acid*, 10-Oxostearic acid, $CH_3[CH_2]_7CO(CH_2)_8 . CO_2H$, melts at 76°. It is obtained from stearolic acid (p. 287) by the action of concentrated sulphuric acid. Consult oleic acid, page 285, for the decomposition of its oxime.

9-*Ketostearic Acid*, $CH_3[CH_2]_8CO[CH_2]_7CO_2H$, melts at 83°. It is obtained from chlorketostearic acid (B. **29**, 806), a transposition product of ricinoleic acid (p. 286).

B. UNSATURATED KETONIC ACIDS. OLEFINE KETONIC ACIDS.

β-Ketonic Acids:

Ethidene Aceto-acetic Ester, $CH_3 . CH : C<\begin{matrix}CO . CH_3\\ CO_2C_2H_5\end{matrix}$, results from the action of hydrochloric acid upon aldehyde and acetoacetic ester. It boils at 211° (A. **218**, 172; B. **29**, 172).

γ-Ketonic Acids:

β-**Aceto-acrylic Acid**, $CH_3 . CO . CH : CH . CO_2H$, is derived together with β-hydroxylævulinic acid from β-bromlævulinic acid and also from *chloralacetone* upon digestion with a soda solution. It melts at 125° C. It combines with HBr and with bromine, forming αβ-dibrom-lævulinic acid, and α-bromlævulinic acid (A. **264**, 234).

β-**Trichlor-aceto-acrylic Acid**, $CCl_3 . CO . CH : CH . CO_2H$, or $CCl_3 . \overline{C(OH)CH : CHCOO}$, *Trichlorphenomalic Acid*. It is obtained from benzene by the action of potassium chlorate and sulphuric acid (A. **223**, 170; **239**, 176). It melts at 131°. It breaks up into chloroform and maleïc acid when boiled with barium hydroxide.

It yields acetyl trichlorphenomalic acid, $CCl_3\overline{C(OCOCH_3 .)CH : CH . COO}$, melting at 86° (A. **254**, 152), when treated with acetic anhydride. *Perchloracetyl Acrylic Acid*, $CCl_3 . COCCl : CCl . CO_2H$, melting at 83–84° (B. **26**, 511), and other chlorinated acetyl-acrylic, and acetyl methyl acrylic acids (B. **26**, 1670), are formed from the decomposition of benzene derivatives which have previously been chlorinated.

β-Acetyl-dibrom-acrylic Acid, $CH_3 . COCBr : CBr . COOH$, or $CH_3 . C(OH)CBr : CBrCOO$, melting at 78°, results upon treating *a* tribromthiotolene with nitric acid. Its remarkably low conductivity bespeaks its lactone formula (B. **24**, 77; **26**, R. 16).

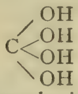
δ-**Ketonic Acids.**—Chlorinated *δ*-ketonic acids have been obtained from the ketochlorides of resorcinol and orcinol, *e. g.*, trichloracetyl-trichlorcrotonic acid, $CCl_3 . CO . CCl : CH . CCl_2 . CO_2H$, see B. **26**, 317, 594, 1666.

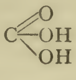
CARBONIC ACID AND ITS DERIVATIVES.

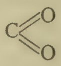
The acid only exists in its salts and esters, and may be regarded as oxyformic acid, $HO . CO . OH$. Its symmetrical structure distinguishes it, however, from the other oxy-acids containing three atoms of oxygen. It is a weak *dibasic* acid and constitutes the transition to the true dibasic dicarboxylic acids—hence it will be treated separately.

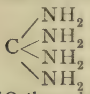
On attempting to liberate the hydrated acid from carbonates by a stronger acid, it breaks down, as almost always happens, when two hydroxyl groups are attached to the same carbon atom. A molecule of water separates, and carbon dioxide, CO_2, the anhydride of carbonic acid, is set free. The carbonates recall the sulphites in their deportment, and carbon dioxide reminds us of sulphur dioxide or sulphurous anhydride.

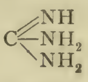
Every carbon compound, containing an atom of carbon in double union with an oxygen atom, may be regarded as the anhydride of a dihydroxyl body corresponding to it. The hydrate formula, $C = O(OH)_2$, of carbonic acid may be viewed as the formula of an anhydride of the compound $C(OH)_4$. Of course a compound of this form will be as unstable as orthoformic acid, $HC(OH)_3$ (p. 224). However, esters derived from the formula $C(OH)_4$, can actually be prepared; they are the *orthocarbonic esters*. In a broader sense, all methane derivatives, in which the four hydrogen atoms have been replaced by four univalent elements or residues, must be considered as derivatives of orthocarbonic acid, *e. g.*, tetrachlor-, tetrabrom-, tetra-iodo-, and tetrafluormethane. From this point of view tetrachlormethane is the chloride of orthocarbonic acid. These compounds, together with chloropicrin, CCl_3NO_2, bromopicrin, CBr_3NO_2, brom-nitroform, $CBr(NO_2)_3$, and tetranitromethane, $C(NO_2)_4$, will be discussed later as derivatives of orthocarbonic acid. The carbon tetramide is not known. Ammonia appears most frequently in the reactions where it might well be expected, and also guanidine, which sustains the same relation to the hypothetical carbon tetramide—the amide of orthocarbonic acid, as metacarbonic acid bears to the ortho-acid:


Orthocarbonic Acid,
Does not exist


Metacarbonic Acid,
Does not exist


Carbon Dioxide,
Carbonic Acid Anhydride.

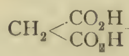

Amide of Orthocarbonic Acid,
Does not exist


Guanidine.

Carbon Monoxide, CO, the first oxidation product of carbon, was described immediately after formic acid.

Carbon Dioxide, CO_2, is the final combustion product of carbon. Under favorable conditions the carbon of every organic substance will be converted into it. Carbon in the quantitative analysis of carbon derivatives is determined in the form of CO_2.

Several methods for the formation of carbonic acid, which are especially important in organic chemistry, may be mentioned here. Carbonic acid is developed from fermentable sugars in the alcoholic fermentation process (p. 119). Carbonic acid is readily formed by the oxidation of formic acid (p. 224), into which it can be converted by reduction (B. **28**, R. 458). Carbon dioxide can be withdrawn from the carbonic acids, *i. e.*, from the acids containing carboxyl, $-C\begin{smallmatrix}/OH\\ \backslash\backslash O\end{smallmatrix}$, when hydrogen will enter where the carboxyl group was first attached. Those polycarbonic acids, containing two carboxyl groups in union with each other, or two and more carboxyls linked to the same carbon atom, readily part with carbon dioxide on the application of heat. In the latter case carboxylic acids result, in which each carboxyl remaining over is attached to a particular carbon atom, *e. g.*:

Malonic Acid, 

$$CH_2<\begin{matrix}CO_2H\\CO_2H\end{matrix} \longrightarrow CO_2 \text{ and } CH_3.CO_2H.$$

The β-ketonic acids deport themselves similarly (p. 371), *e. g.*:

$$\text{Acetoacetic Acid, } CH_3.CO.CH_2.CO_2H \longrightarrow CO_2 \text{ and } CH_3.CO.CH_3.$$

Monocarboxylic acids or their alkali salts can be deprived of CO_2 upon heating them with NaOH, when it disappears as CO_3Na_2 (p. 81):

$$CH_3.CO_2Na + NaOH = CO_3Na_2 + CH_4.$$

The electric current acting upon concentrated solutions of the alkali salts of carboxylic acids splits off carbon dioxide (p. 83), *e. g.*:

$$2CH_3.CO_2K \longrightarrow \overbrace{CH_3CH_3 + 2CO_2}^{+} \text{ and } 2K.$$

The calcium salts of many carboxylic acids are decomposed by heat with the production of calcium carbonate and ketones (p. 188), *e. g.:*

$$(CH_3CO_2)_2Ca \longrightarrow CO_3Ca + CH_3 . CO . CH_3.$$

These and similar reactions, in which CO_2 is easily split off from organic compounds, are of the first importance in the production of the different classes of compounds. In contrast to the splitting-off of CO_2 in certain reactions we have its absorption by certain organic alkali derivatives: nucleus-syntheses, in which carboxylic acids are produced:

$$CH_3Na + CO_2 = CH_3 . CO_2Na \text{ (p. 240).}$$

$$C_6H_5ONa + CO_2 = C_6H_4 <^{CO_2Na}_{OH} \text{ (compare salicylic acid).}$$

Esters of Metacarbonic Acid, or ordinary Carbonic Acid.

The *primary esters* of carbonic acid are not stable in a free condition.

Dumas and Peligot obtained the barium salt of methyl carbonic acid on conducting carbonic acid into a methyl alcohol solution of anhydrous baryta (A. **35**, 283).

The potassium salt of **Ethyl Carbonic Acid**, $CO <^{O . C_2H_5}_{OK}$, separates in pearly scales on adding CO_2 to the alcoholic solution of potassium alcoholate. Water decomposes it into potassium carbonate and alcohol.

The *neutral esters* appear (1) when the alkyl iodides act on silver carbonate:

$$CO_3Ag_2 + 2C_2H_5I = CO_3(C_2H_5)_2 + 2AgI;$$

also (2) by treating esters of chlorformic acid with alconols, whereby *mixed* esters may also be obtained:

$$CO <^{Cl}_{O . CH_3} + C_2H_5 . OH = \underset{\text{Methyl-ethyl Carbonate.}}{CO <^{O . C_2H_5}_{O . CH_3}} + HCl.$$

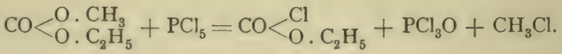
It is also true, that, with application of heat, the higher alcohols are able to expel the lower alcohols from the mixed esters:

$$\underset{\text{Methyl Ethyl Ester}}{CO <^{O . C_2H_5}_{O . CH_3}} + C_2H_5 . OH = \underset{\text{Diethyl Ester.}}{CO <^{O . C_2H_5}_{O . C_2H_5}} + CH_3OH.$$

Hence, to obtain the mixed ester, the reaction must occur at a lower temperature.

As regards the nature of the product, it is immaterial as to what order is pursued in introducing the alkyl groups, *i. e.*, whether proceeding from chlorformic ester, we let ethyl alcohol act upon it, or reverse the case, letting methyl alcohol act upon ethyl chlorformic ester; the same methyl ethyl carbonic acid results in each case (B. **13**, 2417). This is an additional confirmation of the like valence of the carbon affinities, already proved by numerous experiments made with that direct object (with the mixed ketones) in view.

The neutral carbonic esters are ethereal smelling liquids, dissolving readily in water. Excepting dimethyl and the methyl-ethyl ester, all are lighter than water. With ammonia they first yield carbamic esters and then urea. When they are heated with phosphorus pentachloride, an alkyl group is eliminated, and in the case of the mixed esters this is always the lower one, while the chlorformic esters constitute the product:



$$CO\begin{matrix}<\end{matrix}\begin{matrix}O.CH_3\\O.C_2H_5\end{matrix} + PCl_5 = CO\begin{matrix}<\end{matrix}\begin{matrix}Cl\\O.C_2H_5\end{matrix} + PCl_3O + CH_3Cl.$$

Methyl Carbonic Ester, $CO_3(CH_3)_2$, is produced from chlorformic ester by heating with lead oxide. It boils at 91°. The **methyl ethyl ester,** $CO_3\begin{matrix}<\end{matrix}\begin{matrix}CH_3\\C_2H_5\end{matrix}$, boils at 109°. The **ethyl ester,** $CO_3(C_2H_5)_2$, is obtained from ethyl oxalate, $C_2O_4(C_2H_5)_2$, on warming with sodium or sodium ethylate (with evolution of CO_2). It boils at 126°. The *methyl propyl ester*, $CO_3(CH_3)(C_3H_7)$, boils at 131°.

The *ethylene ester*, $CO_3C_2H_4$, glycol carbonate, obtained from glycol and $COCl_2$, melts at 39° and boils at 236°.

Derivatives of Orthocarbonic Acid (p. 383).

Orthocarbonic Ester, $C(O.C_2H_5)_4$ (1864 Bassett, A. **132**, 54), may be regarded as the ether of the tetrahydric alcohol or normal carbonic acid, $C(OH)_4$. It is produced when sodium ethylate acts on chloropicrin:

$$CCl_3(NO_2) + 4C_2H_5.ONa = C(O.C_2H_5)_4 + 3NaCl + NO_2Na.$$

It is a liquid with an ethereal odor, and boils at 158–159°. When heated with ammonia it yields guanidine and alcohol.

The *propyl ester*, $C(O.C_3H_7)_4$, boils at 224°, the *isobutyl ester* at 250°, and it seems the *methyl ester* can not be prepared (A. **205**, 254).

The tetrahalogen substitution products of methane appear to be the halides corresponding to orthocarbonic acid. They bear the same relation to the orthocarbonic esters that chloroform, bromoform and iodoform sustain to the orthoformic esters. However, the orthocarbonic acid esters have not yet been prepared from the tetrahalogen substitution products of methane. Several nitrohalogen methanes and tetranitro-methane will be described here.

Methane Tetrahalogen Substitution Products:

Tetrafluormethane, Carbon Tetrafluoride, CF_4, is a colorless gas, condensable by pressure. It is remarkable that this body belongs to that small class of carbon derivatives which can be directly prepared from the elements. Finely divided carbon, *e. g.*, lamp black, combines directly with fluorine, with production of light and heat, and yields CF_4.

Tetrachlormethane or Carbon Tetrachloride, CCl_4, is formed (1) by the action of chlorine upon chloroform in sunlight, or upon the addition of iodine, and (2) by action of Cl upon CS_2 at 20–40°, C_2Cl_4 and C_2Cl_6 being formed at the same time (B. **27**, 3160); (3) upon heating CS_2 with S_2Cl_2 in the presence of small quantities of iron: $CS_2 + 2S_2Cl_2 = CCl_4 + 6S$ (D. R. P. 72999).

It is a pleasant-smelling liquid, boiling at 76°. Its specific gravity is 1.631 at 0°. At —30° it solidifies to a crystalline mass. It is an excellent solvent for many substances, and is made upon a technical scale. Heated with alcoholic KOH, it decomposes according to the following equation:

$$CCl_4 + 6KOH = K_2CO_3 + 3H_2O + 4KCl.$$

CCl_4 sustains the same relation to carbonic acid that chloroform does to formic acid. When the vapors are conducted through a red-hot tube, decomposition occurs; C_2Cl_4 and C_2Cl_6 are produced.

This is an interesting reaction because, as we learned under acetic acid (p. 274), it plays a part in the first synthesis of this long-known acid. When carbon tetrachloride is digested with phenols and sodium hydroxide, *phenol carboxylic acids* are produced.

Tetrabrommethane, CBr_4, obtained by the action of brom-iodide upon bromoform or CS_2, crystallizes in shining plates, melting at 92.5°, and boiling, with but little decomposition, at 189°.

Tetraiodomethane, CI_4, carbon iodide, is formed when CCl_4 is heated with aluminium iodide. It crystallizes from ether in dark red, regular octahedra, of specific gravity 4.32 at 20°. On exposure to air it decomposes into CO_2 and I. Heat accelerates the decomposition.

Nitro-derivatives of Orthocarbonic Acid.

Nitrochloroform, $C(NO_2)Cl_3$—Chloropicrin, trichlor-nitromethane, is frequently produced in the action of nitric acid upon chlorinated carbon compounds (chloral), and also when chlorine or bleaching powder acts upon nitro-derivatives (fulminating mercury, picric acid and nitromethane; also from fulminating mercury, p. 238).

In the preparation of chloropicrin, 10 parts of freshly prepared bleaching powder are mixed to a thick paste with cold water and placed in a retort. To this is added a saturated solution of picric acid, heated to 30°. Usually the reaction occurs without any additional heat, and the chloropicrin distils over with the aqueous vapor (A. 139, 111).

Chloropicrin is a colorless liquid, boiling at 112°, and having a specific gravity of 1.692 at 0°. It possesses a very penetrating odor that attacks the eyes powerfully. It explodes when rapidly heated. When treated with acetic acid and iron filings it is converted into methylamine:

$$CCl_3(NO_2) + 6H_2 = CH_3.NH_2 + 3HCl + 2H_2O.$$

Alkaline sulphites change it to formyl trisulphonic acid, ammonia to guanidine, and sodium ethylate to orthocarbonic ester (p. 386).

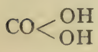
Bromopicrin, $CBr_3(NO_2)$, melting at + 10°, can be distilled under greatly reduced pressure without decomposition, and is formed, like the preceding chloro-compound, by heating picric acid with calcium hypobromite (calcium hydroxide and bromine), or by heating nitromethane with bromine (p. 157). It closely resembles chloropicrin.

Brom-nitroform, $C(NO_2)_3Br$, Brom-trinitromethane, is produced by permitting bromine to act for several days upon nitroform exposed to sunlight. The reaction takes place more rapidly by adding bromine to the aqueous solution of the mercury salt of nitroform. In the cold it solidifies to a white crystalline mass, fusing at +12°. It volatilizes in steam without decomposition.

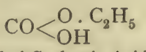
Tetranitromethane, $C(NO_2)_4$, results on heating nitroform with a mixture of fuming nitric acid and sulphuric acid. It is a colorless oil that solidifies to a crystalline mass, fusing at 13°. It is insoluble in water, but dissolves readily in alcohol and ether. It is very stable, and does not explode on application of heat, but distils at 126°.

CHLORIDES AND AZIDES OF CARBONIC ACID.

Two series of salts, two series of esters, and two chlorides can be obtained theoretically from a dibasic acid:

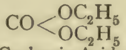


$CO<\substack{OH\\OH}$



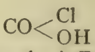
$CO<\substack{O\,.\,C_2H_5\\OH}$

Ethyl Carbonic Acid, only known as salt



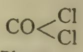
$CO<\substack{OC_2H_5\\OC_2H_5}$

Carbonic Acid, Diethyl Ester



$CO<\substack{Cl\\OH}$

Chlorcarbonic Ester, only as ester



$CO<\substack{Cl\\Cl}$

Phosgene.

(1) **Chlorcarbonic Ester.**—The primary chloride of carbonic acid, *chlorcarbonic acid*, is not known, because it splits off HCl too easily. Its esters are, however, known. They are produced when alcohols act upon phosgene, the secondary chloride of carbonic acid, carbon-oxychloride (Dumas, 1833). They are often called chlorformic esters, because they can be regarded as esters of the chlorine substitution products of formic acid:

$$COCl_2 + C_2H_5OH = Cl\,.\,COOC_2H_5 + HCl.$$

They are most readily prepared by introducing the alcohol into liquid and strongly cooled phosgene (B. **18**, 1177). They are volatile, disagreeable-smelling liquids, decomposable by water. When heated with anhydrous alcohols they yield the neutral carbonic esters; with ammonia they yield urethanes (p. 394); with hydrazine, hydrazi-carbonic esters (p. 405); with ammonium hydronitride, nitrogen esters of carbonic acid (p. 389). They contain the group COCl, just as in acetyl chloride; hence they behave like fatty acid chlorides.

The **methyl ester**, $CClO\,.\,O\,.\,CH_3$, boils at 71.4°; the **ethyl ester**, $CClO_2\,.\,C_2H_5$, at 93°; sp. gr. 1.14396 (15°); the **propyl ester** at 115°, the **isobutyl ester** at 128.8°, and the **isoamyl ester** at 154° (B. **13**, 2417; **25**, 1449).

Perchlorcarbonic Ethyl Ester, $Cl\,.\,CO\,.\,OC_2Cl_5$, melting at 26° and boiling at 209° under ordinary pressure, at 83° (10 mm.), sp. gr. 1.73702, is isomeric with perchloracetic methyl ester (p. 275; A. **273**, 56).

(2) **Carbonyl Chloride,** $COCl_2$, Phosgene Gas, Carbon Oxychloride, boiling at +8°, was first obtained by Davy, in 1812, by the direct union of CO with Cl_2 in sunlight; hence the name phosgene, from φῶς, light, and γεννάω, to produce. It is also formed by conducting CO into boiling $SbCl_5$, and by oxidizing chloroform by air in the sunlight or with chromic acid:

$$2CHCl_3 + CrO_3 + 2O = 2COCl_2 + H_2O + CrO_2Cl_2.$$

Phosgene is most conveniently prepared from carbon tetrachloride (100 c.c.), and 80 per cent. "Oleum" (120 c.c.), a sulphuric acid containing SO_3 (B. **26**, 1990), when the SO_3 is converted into pyrosulphuryl chloride, $S_2O_5Cl_2$.

Technically it is made by conducting CO and Cl_2 over pulverized and cooled bone charcoal (Paternò). Instead of condensing the gas it may be collected in cooled benzene.

Carbonyl chloride is a colorless gas with suffocating odor, and on cooling is condensed to a liquid. *Transpositions:* (1) Water at once breaks it up into CO_2 and 2HCl. (2) Alcohols convert it into chlorcarbonic and carbonic esters. (3) With ammonium chloride it forms *urea chloride.* (4) Urea is produced when ammonia acts upon it. Phosgene has been employed in numerous nucleus-synthetic reactions, *e. g.*, it has been used in the technical way for the preparation of di- and tri-phenylmethane dye-stuffs (see tetra-methyl-diamido-benzophenone).

Carbon Oxychlorbromide, COClBr, boiling at 35–37°, and carbon oxybromide, $COBr_2$, boiling at 63–66°, are formed when $COCl_2$ and PBr_3 interact at 150° (B. **28**, R. 148).

The nitrogen carbonic esters and nitrogen carbon monoxide correspond to the chlorcarbonic esters.

Nitrogen Carbonic Methyl Ester, Azide Carbonic Ester, $N_3 . CO_2C_2H_5$, boiling at 102°, is a transparent liquid, produced by the action of chlorcarbonic ester upon ammonium hydronitride (J. pr. Ch. [2] **52**, 461).

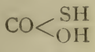
Nitrogen Carbon Monoxide, $CO(N_3)_2$, consists of explosive crystals, very volatile, with a penetrating and stupefying odor, recalling both hydronitric acid and carbon oxychloride. It is produced when sodium nitrite acts upon the hydrochloride of carbohydrazide:

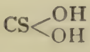
$$CO(NH . NH_2 . HCl)_2 + 2NO_2Na = CO(N_3)_2 + 2NaCl + 4H_2O.$$

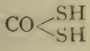
Its aqueous solution decomposes into carbon dioxide and hydrazoic acid (B. **27**, 2684; J. pr. Ch. [2] **52**, 282).

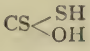
SULPHUR DERIVATIVES OF ORDINARY CARBONIC ACID.

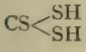
By supposing the oxygen in the formula $CO(OH)_2$ to be replaced by sulphur, there result:

1.  $\mathrm{CO}<^{\mathrm{SH}}_{\mathrm{OH}}$ **Thiocarbonic Acid** **Carbon-monothiol Acid**

2.  $\mathrm{CS}<^{\mathrm{OH}}_{\mathrm{OH}}$ **Sulphocarbonic Acid** **Thion-carbonic Acid**

3.  $\mathrm{CO}<^{\mathrm{SH}}_{\mathrm{SH}}$ **Dithiocarbonic Acid** **Carbondithiol Acid**

4.  $\mathrm{CS}<^{\mathrm{SH}}_{\mathrm{OH}}$ **Sulphothiocarbonic Acid** **Thion-carbon-thiol Acid**

5.  $\mathrm{CS}<^{\mathrm{SH}}_{\mathrm{SH}}$ **Trithiocarbonic Acid.**

The doubly-linked *S* is indicated in the name by *sulph* or *thion*, while it is *thio* or *thiol* when it is singly linked.

The free acids are not known, or are very unstable. Numerous derivatives, such as salts, esters and amides, are known. Carbon oxysulphide, COS, is the anhydride or sulphanhydride corresponding to thiocarbonic acid, sulphocarbonic acid and dithiocarbonic acid.

Carbon disulphide, CS_2, sustains the same relation to sulphothiocarbonic acid and trithiocarbonic acid that carbon dioxide does to ordinary carbonic acid.

Phosgene corresponds to thiophosgene, $CSCl_2$.

The two anhydrides, COS and CS_2, will be first discussed, then the salts and esters of the five acids just mentioned, to which thiophosgene and the sulphur derivatives of the chlorcarbonic esters attach themselves.

Carbon Oxysulphide, COS (1867 C. v. Than, A. Spl. **5**, 245), occurs in some mineral springs, and is formed (1) by conducting sulphur vapor and carbon monoxide through red-hot tubes. (2) On heating CS_2 with SO_3. (3) By the action of $COCl_2$ upon CdS at 260–280° (B. **24**, 2971). It is most easily prepared (4) by heating potassium thiocyanate with sulphuric acid, diluted with an equal volume of water: $CN.SH + H_2O = CSO + NH_3$ (B. **20**, 550), or with fatty acids.

In order to obtain it pure, conduct the gas into an alcoholic potash solution, and (5) decompose the separated potassium ethyl thiocarbonate, $CO<^{O.C_2H_5}_{SK}$, with dilute hydrochloric acid.

Carbon oxysulphide is a colorless gas, with a faint and peculiar odor. It inflames readily, and forms an explosive mixture with air. It is soluble in an equal volume of water. It is decomposed by the alkalies according to the following equation:

$$COS + 4KOH = CO_3K_2 + K_2S + 2H_2O.$$

Carbon Disulphide, CS_2, boiling at 47°, was first obtained in 1796 by Lampadius, when he distilled pyrite with carbon. It is at present obtained by conducting sulphur vapor over ignited charcoal, and is one of the few carbon compounds which can be prepared by the direct union of carbon with other elements. It is a colorless liquid with strong refractive power, and at 0° has a specific gravity of 1.297. It is obtained pure by distilling the commercial product over mercury or mercuric chloride; its odor is then very faint. It is almost insoluble in water, but mixes with alcohol and ether. It serves as an excellent solvent for iodine, sulphur, phosphorus, fatty oils and resins, and is used in the vulcanization of rubber. In the cold it combines with water, yielding the hydrate $2CS_2 + H_2O$, which decomposes again at —3°.

Carbon disulphide, in slight amount, is detected by its conversion into potassium xanthate. This is accomplished by means of alcoholic potash. The copper salt is obtained from the potassium compound. The production of the bright-red compound of CS_2 with triethyl phosphine (p. 174, and B. **13**, 1732) is a more delicate test. Compare also the mustard-oil reaction, p. 166.

H_2S and CS_2 conducted over heated copper yield methane (p. 81). Carbon disulphide is tolerably stable toward dry halogens, so that frequently it is used as a solvent in adding halogens to unsaturated carbon compounds.

However, chlorine gas converts CS_2 into thiocarbonyl chloride, $CSCl_2$, and in the presence of iodine into $CSCl_4 = CCl_3.SCl$, perchlormethyl mercaptan and S_2Cl_2; finally into CCl_4 (p. 386). Alcoholates change it into xanthates. Zinc and hydrochloric acid convert CS_2 into trithiomethylene.

Thiocarbonic Acid.—The salts and esters of all these acids, which when free are exceedingly unstable, may be produced (1) by the union of the anhydrides, CO_2, COS, CS_2, with (*a*) the sulphides of the alkali and alkaline earth metals, (*b*) the mercaptides of the alkali metals, (*c*) and of the last two with alcoholates; (2) by the transposition of the salts thus obtained with alkylogens and alkylen dihalides; (3) by the action of alcohols and alcoholates, mercaptans and alkali mercaptides upon $COCl_2 . Cl . CO_2C_2H_5$ (p. 388), $CSCl_2$ and $Cl . CS_2C_2H_5$ (p. 393).

Monothiocarbonic Acids:

1. **Ethyl Thiocarbonic Acid.**—Ethyl carbon-mono-thiol Acid, $HS . CO . OC_2H_5$. The *potassium salt*, $CO<\begin{matrix}O . C_2H_5\\SK\end{matrix}$, is obtained (1) from xanthic esters and alcoholic potash (p. 392), and (2) in the union of carbon dioxide with potassium mercaptide. It crystallizes in needles and prisms, which readily dissolve in water and alcohol. With ethyl iodide the potassium salt forms *ethyl thioxycarbonate*, $CO<\begin{matrix}O . C_2H_5\\S . C_2H_5\end{matrix}$, which can be prepared from chlorcarbonic ester, $COCl . O . C_2H_5$, and sodium or zinc mercaptide. It boils at 156°. Alkalies decompose it into carbonate, alcohol and mercaptan (B. **19**, 1227).

2. **Sulphocarbonic Acid.**—Thion-carbonic Acid, $HO . CS . OH$. Its *ethyl ester*, $CS(O . C_2H_5)_2$, is produced by the action of sodium alcoholate upon thiocarbonyl chloride, $CSCl_2$, and in the distillation of $S_2(CS . O . C_2H_5)_2$. It is an ethereal smelling liquid, boiling at 161°. With alcoholic ammonia the ester decomposes into alcohol and ammonium thiocyanate, $CN . S . NH_4$.

Dithiocarbonic Acids.

3. *Dithiocarbonic Acid*, Carbon-dithiol Acid, $CO(SH)_2$. The free acid is not known.

The *methyl ester*, $CO(S . CH_3)_2$, boils at 169°; the *ethyl ester*, $CO(S . C_2H_5)_2$, at 196°. These result (1) when $COCl_2$ acts upon the mercaptides:

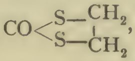
$$COCl_2 + 2C_2H_5 . SK = CO(S . C_2H_5)_2 + 2KCl;$$

and (2) when thiocyanic esters (p. 423) are heated with concentrated sulphuric acid:

$$2CN . S . CH_3 + 3H_2O = CO(S . CH_3)_2 + CO_2 + 2NH_3.$$

They are liquids with garlicky odor. Alcoholic ammonia decomposes them into urea and mercaptans:

$$CO(S . C_2H_5)_2 + 2NH_3 = CO<\begin{matrix}NH_2\\NH_2\end{matrix} + 2C_2H_5 . SH.$$

Ethylene Dithiocarbonic Ester,  $CO<\begin{matrix}S-CH_2\\ \quad\;\, |\\S-CH_2\end{matrix}$, from trithiocarbonic ethylene ester, melts at 31°.

4. *Sulphothiocarbonic Acid*, Thion-carbon-thiol Acid, $HO . CS . SH$, does not exist free. The *xanthates*, $R . O . C . SSMe$, discovered by Zeise in 1824, are obtained from it.

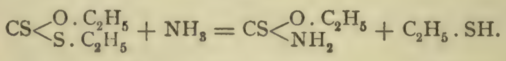
The **xanthates** are produced by the combined action of CS_2 and caustic alkalies in alcoholic solution—*e. g.*, potassium xanthate, consisting of yellow, silky needles, which crystallize:

$$CS_2 + KOH + C_2H_5 . OH = CS<\begin{matrix}O . C_2H_5\\SK\end{matrix} + H_2O.$$

Potassium Ethylxanthate.

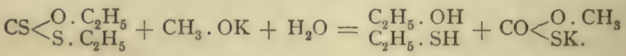
Cupric salts precipitate *yellow* copper salts from solutions of the alkaline xanthates. The acid owes its name, ξανθός, yellow, to this characteristic. By the action of alkyl iodides upon the salts we obtain the esters.

The latter are liquids with garlicky odor, and are not soluble in water. Ammonia breaks them up into mercaptans and esters of sulphocarbamic acid (p. 406):



$$\mathrm{CS}<^{O\,.\,C_2H_5}_{S\,.\,C_2H_5} + NH_3 = \mathrm{CS}<^{O\,.\,C_2H_5}_{NH_2} + C_2H_5\,.\,SH.$$

With alkali alcoholates, mercaptan and alcohol separate, and salts of the alkyl thiocarbonic acids (p. 391) are formed (B. **13**, 530):



$$\mathrm{CS}<^{O\,.\,C_2H_5}_{S\,.\,C_2H_5} + CH_3\,.\,OK + H_2O = \begin{matrix} C_2H_5\,.\,OH \\ C_2H_5\,.\,SH \end{matrix} + \mathrm{CO}<^{O\,.\,CH_3}_{SK.}$$

Xanthic Acid, or ethyl oxydithiocarbonic acid, $C_2H_5\,.\,O\,.\,CS\,.\,SH$. A heavy liquid, not soluble in water. It decomposes at 25° into alcohol and CS_2.

Xanthic Disulphide, $\begin{matrix} S\,.\,CS\,.\,O\,.\,C_2H_5 \\ | \\ S\,.\,CS\,.\,O\,.\,C_2H_5 \end{matrix}$, is produced on adding an alcoholic solution of iodine to the potassium salt just as acetyl sulphide is obtained from thiacetic acid (p. 262). Insoluble, shining needles, melting at 28°.

The *ethyl ester*, $C_2H_5\,.\,O\,.\,CS\,.\,S\,.\,C_2H_5$, is a colorless oil, boiling at 200°.

Ethyl-methyl xanthic ester, $CH_3O\,.\,CS\,.\,S\,.\,C_2H_5$, and methyl xanthic ester, $C_2H_5\,.\,O\,.\,CS\,.\,S\,.\,CH_3$, both boil at 184°. They are distinguished by their behavior toward ammonia and sodium alcoholate (see above).

5. **Trithiocarbonic Acid**, $CS_3H_2 = \mathrm{CS}<^{SH}_{SH}$. Hydrochloric acid precipitates this as a reddish-brown, oily liquid, from solutions of its alkali salts. It is insoluble in water and is very unstable. The alkali salts, when acted upon by the corresponding halogen compounds, yield the following esters:

Ethyl Trithiocarbonate, $\mathrm{CS}<^{S\,.\,C_2H_5}_{S\,.\,C_2H_5}$, boils at 240° with decomposition. The *methyl ester*, $CS(S\,.\,CH_3)_2$, boils at 204–205°. The *ethylene ester*, $\mathrm{CS}<^{S}_{S}>C_2H_4$, melts at 39.5°. When oxidized with dilute nitric acid the ester becomes ethylenedithiocarbonic ester, $COS_2 : C_2H_4$ (A. **126**, 269).

Chlorides of the Sulpho-carbonic Acids: *Thiophosgene*, Thiocarbonyl Chloride, $CSCl_2$, boiling at 73°, sp. gr. 1.508 (15°), is produced when chlorine acts upon carbon disulphide, and when the latter is heated with PCl_5 in closed tubes to 200°: $CS_2 + PCl_5 = CSCl_2 + PCl_3S$.

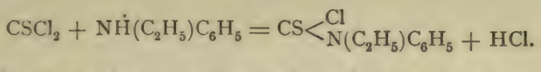
It is most readily obtained by reducing perchlormethylmercaptan, $CSCl_4$ (p. 393), with stannous chloride, or tin and hydrochloric acid (B. **20**, 2380; **21**, 102):

$$CSCl_4 + SnCl_2 = CSCl_2 + SnCl_4.$$

This is the method employed for its production in large quantities.

It is a pungent, red-colored liquid, insoluble in water. On standing exposed to sunlight it is converted into a polymeric, crystalline compound, $C_2S_2Cl_4 = Cl\,.\,CS\,.\,$-$S\,.\,CCl_3$, methyl perchlor-dithioformate, which melts at 116°, and at 180° reverts to the liquid body (B. **26**, R. 600). Water decomposes thiophosgene into CO_2, H_2S and 2HCl, while ammonia converts it into ammonium sulphocyanide (p. 422).

Thiocarbonyl chloride converts secondary amines (1 molecule) into dialkyl sulphocarbamic chlorides:



$$CSCl_2 + N\dot{H}(C_2H_5)C_6H_5 = CS<\begin{matrix}Cl\\N(C_2H_5)C_6H_5\end{matrix} + HCl.$$

A second molecule of the amine produces tetra-alkylic thioureas (B. **21**, 102).

Benzene, in the presence of $AlCl_3$, yields thiobenzophenone.

Phosgene and thiophosgene, when acted upon by alcohols and mercaptans, yield sulphur derivatives of chlorcarbonic ester (p. 389).

Chlorcarbon-thiol Ethyl Ester, ...	$Cl . COSC_2H_5$
Chlorthiocarbonic Ethyl Ester, ...	$Cl . CSOC_2H_5$
Chlorperthiocarbonic Ethyl Ester, ...	$Cl . CSSC_2H_5$
Perchlorsulpho-thiocarbonic Methyl Ester, ...	$Cl . CSSCCl_3$ (see thiophosgene).

SULPHUR DERIVATIVES OF ORTHOCARBONIC ACID.

Perchlormethyl Mercaptan, $CCl_3 . SCl$, boiling at 147°, results from the action of chlorine upon CS_2. It is a bright yellow liquid. Stannous chloride reduces it to thiophosgene. Nitric acid oxidizes it to

Trichlormethyl Sulphonic Chloride, $CCl_3 . SO_2Cl$, melting at 135° and boiling at 170°, which can be made by the action of moist chlorine upon CS_2. It is insoluble in water, but dissolves readily in alcohol and ether. Its odor is like that of camphor, and excites tears. Water changes the chloride to

Trichlormethyl Sulphonic Acid, $CCl_3 . SO_3H + H_2O$, consisting of deliquescent crystals. By reduction it yields $CHCl_2 . SO_3H$, dichlormethyl sulphonic acid, $CH_2Cl . SO_3H$, monochlormethyl sulphonic acid, and $CH_3 . SO_3H$ (p. 152).

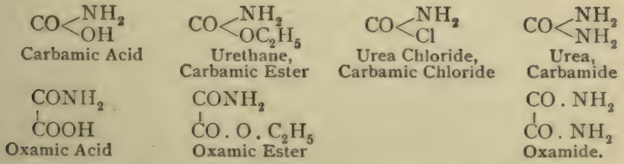
Diethyl Sulphone Dibrom-methane, $CBr_2(SO_2C_2H_5)_2$, melting at 131°, and *diethylsulphone di-iodomethane*, $CI_2(SO_2C_2H_5)_2$, melting at 176°, are formed when bromine acts upon diethyl sulphone methane, and iodine in potassium iodide, or iodine alone upon diethyl sulphone methane potassium (B. **30**, 487).

Potassium Di-iodomethane Disulphonate, $CI_2(SO_3K)_2$, and *Potassium Iodomethane Disulphonate*, $CHI(SO_3K)_2$, are produced when potassium diazomethane disulphonate is decomposed with iodine and with hydrogen iodide. Sodium amalgam reduces both bodies to methylene disulphonic acid (p. 204).

Potassium Methanoltrisulphonate, $HO . C(SO_3K)_3 . H_2O$, results when the addition product of acid potassium sulphite and potassium diazomethane disulphonate is boiled with hydrochloric acid. A like treatment of potassium sulph-hydrazimethylene trisulphonate will also yield it (B. **28**, 2378).

AMIDE DERIVATIVES OF CARBONIC ACID.

Carbonic acid forms amides which are perfectly analogous to those of a dibasic acid—*e. g.*, oxalic acid (p. 432):



$CO<\begin{matrix}NH_2\\OH\end{matrix}$ Carbamic Acid

$CO<\begin{matrix}NH_2\\OC_2H_5\end{matrix}$ Urethane, Carbamic Ester

$CO<\begin{matrix}NH_2\\Cl\end{matrix}$ Urea Chloride, Carbamic Chloride

$CO<\begin{matrix}NH_2\\NH_2\end{matrix}$ Urea, Carbamide

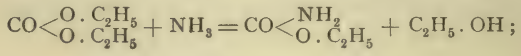
$\begin{matrix}CONH_2\\|\\COOH\end{matrix}$ Oxamic Acid

$\begin{matrix}CONH_2\\|\\CO . O . C_2H_5\end{matrix}$ Oxamic Ester

$\begin{matrix}CO . NH_2\\|\\CO . NH_2\end{matrix}$ Oxamide.

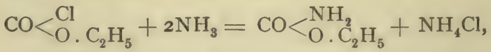
Carbamic Acid, $H_2N . CO . OH$, *Amidoformic Acid*, is not known in a free state. It seems its ammonium salt is contained in commercial ammonium carbonate, and is prepared by the direct union of two molecules of ammonia with carbon dioxide. It is a white mass which breaks up at 60° into $2NH_3$ and CO_2, but these combine again upon cooling. Salts of the earth and heavy metals do not precipitate the aqueous solution ; it is only after warming that carbonates separate, when the carbamate has absorbed water and becomes ammonium carbonate. When ammonium carbamate is heated to 130–140° in sealed tubes, water is withdrawn and urea, $CO(NH_2)_2$, formed.

The *esters* of carbamic acid are called *urethanes;* these are obtained (1) by the action of ammonia at ordinary temperatures upon carbonic esters:

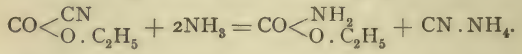


$$\mathrm{CO}<\begin{smallmatrix}O\,.\,C_2H_5\\O\,.\,C_2H_5\end{smallmatrix} + NH_3 = \mathrm{CO}<\begin{smallmatrix}NH_2\\O\,.\,C_2H_5\end{smallmatrix} + C_2H_5\,.\,OH\,;$$

and (2) in the same manner from the esters of chlorcarbonic and cyancarbonic acids:

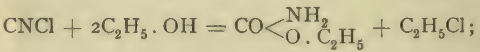


$$\mathrm{CO}<\begin{smallmatrix}Cl\\O\,.\,C_2H_5\end{smallmatrix} + 2NH_3 = \mathrm{CO}<\begin{smallmatrix}NH_2\\O\,.\,C_2H_5\end{smallmatrix} + NH_4Cl,$$



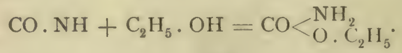
$$\mathrm{CO}<\begin{smallmatrix}CN\\O\,.\,C_2H_5\end{smallmatrix} + 2NH_3 = \mathrm{CO}<\begin{smallmatrix}NH_2\\O\,.\,C_2H_5\end{smallmatrix} + CN\,.\,NH_4.$$

Also (3) by conducting cyanogen chloride into the alcohols:



$$CNCl + 2C_2H_5\,.\,OH = \mathrm{CO}<\begin{smallmatrix}NH_2\\O\,.\,C_2H_5\end{smallmatrix} + C_2H_5Cl\,;$$

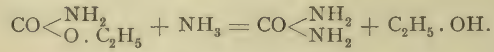
and (4) by the direct union of cyanic acid with the alcohols:



$$CO\,.\,NH + C_2H_5\,.\,OH = \mathrm{CO}<\begin{smallmatrix}NH_2\\O\,.\,C_2H_5\end{smallmatrix}.$$

When there is an excess of cyanic acid employed, allophanic esters are also produced (p. 403).

The urethanes are crystalline, volatile bodies, soluble in alcohol, ether and water. Sodium acts upon their ethereal solution with the evolution of hydrogen ; in the case of urethane it is probable that sodium urethane, $NHNa\,.\,COOC_2H_5$ (B. 23, 2785), is produced. Alkalies decompose them into CO_2, ammonia and alcohols. They yield urea when heated with ammonia:



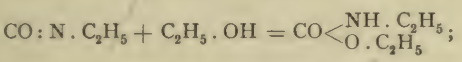
$$\mathrm{CO}<\begin{smallmatrix}NH_2\\O\,.\,C_2H_5\end{smallmatrix} + NH_3 = \mathrm{CO}<\begin{smallmatrix}NH_2\\NH_2\end{smallmatrix} + C_2H_5\,.\,OH.$$

Conversely, on heating urea or its nitrate with alcohols, the urethanes are regenerated.

Methyl Carbamic Ester, $\mathrm{CO}<\begin{smallmatrix}NH_2\\O\,.\,CH_3\end{smallmatrix}$, *methyl urethane*, crystallizes in plates, which melt at 52° and boil at 177°. The *ethyl ester*, $CO(NH_2)\,.\,O\,.\,C_2H_5$, also called **urethane,** consists of large plates, which melt at 50° and boil at 184°. The *propyl ester* melts at 53° and boils at 195°. The *allyl ester*, $CO(NH_2)\,.\,O\,.\,C_3H_5$, is a solid, melting at 21° and boiling at 204°.

Acetyl Urethane, $CH_3\,.\,CONH\,.\,CO_2C_2H_5$, is obtained from acetyl chloride and urethane. It melts at 78° and boils at 130° (72 mm.). Hydrogen in it can be replaced by sodium. Alkyl iodides acting upon the sodium compound produce: alkylic acetyl urethanes (B. **25**, R. 640). When heated to 150° with urea, acetyl urethane passes into acetguanamide, or methyl dioxytriazine, and with hydrazine it yields the triazolones (A. **288**, 318).

The *esters of these alkylized carbamic acids* are formed, like the urethanes, by (1) the action of carbonic or (2) chlorcarbonic esters upon amines; and (3) on heating isocyanic esters (p. 418) with the alcohols to 100°:



$$CO:N.C_2H_5 + C_2H_5.OH = CO{<}\begin{matrix}NH.C_2H_5\\O.C_2H_5\end{matrix};$$

also (4) by the interaction of the chlorides of alkyl urea and the alcohols; (5) when alcohols act upon acid azides (p. 163).

Methyl Etho-carbamic Ester, $CH_3.HN.CO.O.C_2H_5$, boils at 170° (B. **28**, 855).

Ethyl Etho-carbamic Ester, $(C_2H_5)HN.CO.O.C_2H_5$, boils at 175°.

Ethylene Urethane, $C_2H_5.OCO.NHCH_2.CH_2NHCO.O.C_2H_5$, from ethylene diamine and $ClCO_2C_2H_5$ (B. **24**, 2268), melts at 113°.

Derivatives of carbamic acid with *divalent* radicals are produced by the union of esters of the acid with aldehydes:

Ethidene Diurethane, $CH_3.CH(HN.CO.O.C_2H_5)_2$, from urethane and acetaldehyde, crystallizes in shining needles, melting at 126° C. (B. **24**, 2268).

Chloral Urethane, $CCl_3.CH{<}\begin{matrix}OH\\HN.CO.O.C_2H_5\end{matrix}$, from urethane and chloral, melts at 103°. Acid anhydrides convert it into *Trichlorethidene Urethane*, $CCl_3.CH:N.COOC_2H_5$, melting at 143° (B. **27**, 1248).

Urethane Acetic Acid, $CO_2H.CH_2NHCO_2C_2H_5$, is produced on evaporating urethane acetic ester, $C_2H_5OCO.CH_2.NH.CO_2C_2H_5$, with hydrochloric acid. The acid melts at 68°; the ester melts at 24.5–27° and boils at 45° (22 mm.); see nitramine acetic acid, p. 361 (B. **29**, 1681).

Nitrosourethane, $NO.NH.CO_2C_2H_5$, melts at 51° with decomposition. It forms on reducing ammonium nitrourethane with glacial acetic acid and zinc dust (A. **288**, 304).

Nitrosomethyl Urethane, $CO_2C_2H_5N{<}\begin{matrix}CH_3\\NO\end{matrix}$, from methyl urethane and nitrous acid, is a liquid which yields diazomethane when it is digested with methyl alcoholic potash (B. **28**, 855).

Nitrocarbamic Acid, $NO_2.NH.CO_2H$, when liberated by sulphuric acid from its potassium salt, surrounded by ice, breaks down into *nitramide*, $NO_2.NH_2$, melting at 72–85°. and carbon dioxide. The nitramide is extracted by ether. *Potassium Nitrocarbamate*, $NO_2.NH.CO_2K$, consisting of delicate, white needles, is produced when methyl alcoholic potash is allowed to act upon potassium nitrourethane.

Nitrourethane, $NO_2NHCO_2C_2H_5$, melting at 64°, is produced when ethyl nitrate acts upon a cooled sulphuric acid solution of urethane. It dissolves readily in water, and very easily in ether and alcohol, but very sparingly in ligroine. It has a strong acid reaction. Its salts are neutral in their reaction. *Ammonium Nitrourethane*, $NO_2N(NH_4)CO_2C_2H_5$. *Potassium Nitrourethane*, $NO_2NKCO_2C_2H_5$ (J. Thiele and A. Lachmann, A. **288**, 267).

Methyl Nitrourethane, $NO_2N(CH_3)CO_2C_2H_5$, is a colorless oil with an agreeable odor. It is formed when methyl iodide and silver nitrourethane interact, and also from methyl urethane. Ammonia decomposes it into methyl nitramine, p. 171.

Urea Chlorides, Carbamic Acid Chlorides, are produced by the interaction of phosgene gas and ammonium chloride at 400° (B. **20**, 858; **21**, R. 293); by action of $COCl_2$ upon the hydrochlorides of the primary amines at 260–270°, and also upon the secondary amines in benzene solution:

$$COCl_2 + NH_3 . HCl = Cl . CO . NH_2 + 2HCl.$$

Urea Chloride, Carbamic Acid Chloride, Chlorcarbonic Amide, $Cl . CONH_2$, melts at 50° and boils at 61–62°, when it dissociates into hydrochloric acid and isocyanic acid, HCNO. The latter partly polymerizes to *cyamelide*. Urea chloride suffers a like change on standing.

Carbamazide, $N_3 . CO . NH_2$, melting at 97°, is obtained from semicarbazide (p. 405) and nitrous acid. Water decomposes it into CO_2, NH_3, and N_3H (J. pr. Ch. [2] **52**, 467).

Mono-alkyl Urea Chlorides:

Ethyl Urea Chloride, $CO<\begin{matrix}Cl\\NH . C_2H_5\end{matrix}$, also obtained from ethylisocyanate and hydrochloric acid, boils at 92°. *Methyl Urea Chloride*, $CO<\begin{matrix}Cl\\NH . CH_3\end{matrix}$, melts about 90° and boils at 93–94°.

These compounds boil apparently without decomposition, yet they suffer dissociation into hydrochloric acid and isocyanic acid esters, which reunite on cooling: $CO . NR + HCl = CO<\begin{matrix}Cl\\NHR\end{matrix}$.

Dialkyl Urea Chlorides:

Dimethyl Urea Chloride, $CO<\begin{matrix}N(CH_3)_2\\Cl\end{matrix}$, boils at 167° C.

Diethyl Urea Chloride, $CO<\begin{matrix}N(C_2H_5)_2\\Cl\end{matrix}$, is obtained from diethyl oxamic acid by means of PCl_5. It boils at 190–195°.

Deportment: (1) The urea chlorides are decomposed by water into CO_2 and ammonium chlorides. (2) They yield urethanes with alcohols. (3) With amines they form *alkylic ureas:*

$$CO<\begin{matrix}Cl\\NH_2\end{matrix} + C_2H_5 . NH_2 = CO<\begin{matrix}NH . C_2H_5\\NH_2\end{matrix} + HCl.$$

Nucleus-synthetic reactions: (4) With benzene and phenol ethers in the presence of $AlCl_3$ they yield acid amides: $COCl . NH_2 + C_6H_6 = C_6H_5 . CO . NH_2 + HCl$.

Carbamide, Urea, $CO<\begin{matrix}NH_2\\NH_2\end{matrix}$, melting at 132–133°, was discovered by v. Rouelle in urine in 1773, and was first synthesized from isocyanate of ammonium by Wöhler in 1828 (Pogg, A. (1825) **3**, 177; (1828) **12**, 253). This was a brilliant discovery, which showed that organic as well as inorganic compounds could be built up artificially from their elements (p. 17). It occurs in various animal fluids, chiefly in the urine of mammals, and can be separated as nitrate from concentrated urine on the addition of nitric acid. It is present in small quantities in the urine of birds and reptiles. A full-grown man voids upon an average about 30 grams of urea daily. The formation of this substance is due to the decomposition of albuminoid substances. It may be prepared artificially: (1) by evaporating the aqueous solution of ammonium isocyanate, when an atomic transposition occurs (Wöhler):

$$CO:N.NH_4 \text{ yields } CO<^{NH_2}_{NH_2}.$$

Mixed aqueous solutions of potassium cyanate and ammonium sulphate (in equivalent quantities) are evaporated; on cooling, potassium sulphate crystallizes out and is filtered off, the filtrate being evaporated to dryness, and the urea extracted by means of hot alcohol. This is also a reversible process. On heating $\frac{1}{10}$n urea solution for some time to 100°, four to five per cent. of the urea will be changed to ammonium cyanate (B. **29**, R. 829).

It is also formed by the methods in general use in the preparation of acid amides: (2) by the action of ammonia (*a*) upon carbamic esters or urethanes, (*b*) upon alkylic carbonic esters, (*c*) upon fused phenyl carbonate (B. **17**, 1286), and (*d*) upon chlorcarbonic esters. The bodies mentioned under *b*, *c* and *d* first change to carbamic esters:

$$\begin{aligned} NH_2.CO_2C_2H_5 + NH_3 &= NH_2CONH_2 + C_2H_5OH \\ CO(OC_2H_5)_2 + 2NH_3 &= NH_2CONH_2 + 2C_2H_5OH \\ CO(OC_6H_5)_2 + 2NH_3 &= NH_2CONH_2 + 2C_6H_5OH \\ Cl(CO_2C_2H_5) + 3NH_3 &= NH_2CONH_2 + C_2H_5OH + NH_4Cl. \end{aligned}$$

(3) By the action of ammonia upon phosgene and urea chloride:

$$\begin{aligned} COCl_2 + 4NH_3 &= CO(NH_2)_2 + 2NH_4Cl \\ ClCONH_2 + 3NH_3 &= CO(NH_2)_2 + NH_4Cl. \end{aligned}$$

(4) By heating ammonium carbamate or thiocarbamate to 130–140°.

The two following methods of formation show the genetic relation of urea with thiourea, cyanamide and guanidine:

(5) Potassium permanganate oxidizes thiourea to urea. (6) Small quantities of acids convert cyanamide into urea:

$$CN.NH_2 + H_2O = CO<^{NH_2}_{NH_2}.$$

(7) Urea is formed when *guanidine* is boiled with dilute sulphuric acid or baryta water:

$$NH:C(NH_2)_2 + H_2O = CO(NH_2)_2 + NH_3.$$

Urea crystallizes in long, rhombic prisms or needles, which have a cooling taste, like that of saltpetre. It can be readily obtained pure by one recrystallization from amyl alcohol (B. **26**, 2443). It dissolves in one part of cold water and in five parts of alcohol; it is almost insoluble in ether. It melts at 132°, and above that temperature breaks up (1) into ammonia, ammelide, biuret and cyanuric acid. (2) When urea is heated above 100° with water, or when boiled with alkalies or acids, it decomposes into carbon dioxide and ammonia. The same decomposition occurs in the decay of urine.

(3) Nitrous acid decomposes urea, in the same manner that it decomposes all other amides:

$$CO{<}^{NH_2}_{NH_2} + N_2O_3 = CO_2 + 2N_2 + 2H_2O.$$

(4) An alkaline hypobromite decomposes urea into nitrogen, carbon dioxide and water:

$$CO(NH_2)_2 + 3NaOBr = CO_2 + N_2 + 2H_2O + 3NaBr.$$

Salts: Urea, like glycocoll, forms crystalline compounds with acids, bases and salts. Although it is a diamide it combines with but one equivalent of acid (one of the amido-groups is neutralized by the carbonyl group).

Urea Nitrate, $CH_4N_2O \cdot HNO_3$, shining leaflets, which are not very soluble in nitric acid. The *oxalate*, $CO(NH_2)_2C_2H_2O_4 + 2H_2O$, consists of thin leaflets, which are soluble in water.

On evaporating a solution containing both urea and sodium chloride, the compound, $CH_4N_2O \cdot NaCl + H_2O$, separates in shining prisms.

The extent of the decomposition of albuminoid substances in the animal body is one of the fundamental questions of physiology. Urea is by far the most predominant of the nitrogenous decomposition products of albuminous substances in mammalia and batrachia. Its accurate determination is, therefore, of the utmost importance.

The Kjeldahl-Wilfarth method is the best adapted for the estimation of nitrogen in the products of the metabolism. The method of Liebig may also be used for the determination of urea. It consists in titrating in neutral solution with mercuric nitrate, when a precipitate, consisting of a mixture of double compounds of carbamide and mercuric nitrate, separates, together with the simultaneous liberation of nitric acid. The Knop-Hüfner method consists in decomposing the urea with sodium hypobromite (see above). Pflüger and his students have critically examined all methods suggested for this purpose (compare Arch. f. d. ges. Phys. **21**, 248; **35**, 199; **36**, **101**, etc.).

Alkylic ureas are produced according to the same reactions which yield urea (1) when primary or secondary amines act upon isocyanic esters or isocyanic acid:

$$CO:NH + NH_2 \cdot C_2H_5 = \underset{\text{Ethyl Urea.}}{CO{<}^{NH \cdot C_2H_5}_{NH_2}}$$

$$CO = N \cdot C_2H_5 + NH(C_2H_5)_2 = \underset{\text{Triethyl Urea.}}{N(C_2H_5)_2CO \cdot NH \cdot C_2H_5}$$

Alkylic ureas are formed, too, when isocyanic esters are heated with water—CO_2, and amines being produced; the latter unite with the esters:

$$CO:N \cdot C_2H_5 + H_2O = NH_2 \cdot C_2H_5 + CO_2 \text{ and}$$

$$CO:N \cdot C_2H_5 + NH_2 \cdot C_2H_5 = CO{<}^{NH \cdot C_2H_5}_{NH \cdot C_2H_5}.$$

(2) They are also obtained by the action of urea chloride and alkyl-urea chlorides upon ammonia, and primary and secondary amines (p. 396), as well as by the action of phosgene on the latter.

(3) By the action of caustic alkalies on the ureïdes, the urea derivatives containing acid radicals:

$$\underset{\text{Methyl Acetyl Urea}}{\mathrm{CO}{<}\begin{matrix}\mathrm{NH.CO.CH_3}\\\mathrm{NH.CH_3}\end{matrix}} + \mathrm{KOH} = \underset{\text{Methyl Urea.}}{\mathrm{CO}{<}\begin{matrix}\mathrm{NH_2}\\\mathrm{NHCH_3}\end{matrix}} + \mathrm{CH_3CO_2K}.$$

Ureas of this class are perfectly analogous to ordinary urea so far as properties and reactions are concerned. They generally form salts with one equivalent of acid. They are crystalline salts, with the exception of those containing four alkyl groups. On heating those with one alkyl group, cyanic acid (or cyanuric acid) and an amine are produced. The higher alkylized members can be distilled without decomposition. Boiling alkalies convert them all into CO_2 and amines:

$$\mathrm{CO}{<}\begin{matrix}\mathrm{NH.CH_3}\\\mathrm{NH_2}\end{matrix} + \mathrm{H_2O} = \mathrm{CO_2} + \mathrm{NH_3} + \mathrm{NH_2.CH_3}.$$

(4) By desulphurizing the alkylic thio-ureas with an alcoholic silver nitrate solution (B. 28, R. 915).

Methyl Urea, $\mathrm{CO}{<}\begin{matrix}\mathrm{NH.CH_3}\\\mathrm{NH_2}\end{matrix}$, results on heating methyl aceto-urea (from acetamide by the action of bromine and caustic potash) with potassium hydroxide. It melts at 102°.

Ethyl Urea, $\mathrm{CO}{<}\begin{matrix}\mathrm{NH.C_2H_5}\\\mathrm{NH_2}\end{matrix}$, melts at 92°.

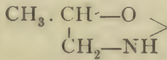
a-**Diethyl Urea,** $\mathrm{CO}{<}\begin{matrix}\mathrm{NH.C_2H_5}\\\mathrm{NH.C_2H_5}\end{matrix}$, melts at 112° and boils at 263°.

β-**Diethyl Urea,** $\mathrm{CO}{<}\begin{matrix}\mathrm{NH_2}\\\mathrm{N(C_2H_5)_2}\end{matrix}$, melts at 70°.

Triethyl Urea, $\mathrm{CO}{<}\begin{matrix}\mathrm{NH.C_2H_5}\\\mathrm{N(C_2H_5)_2}\end{matrix}$, melts at 63° and boils at 223°.

Tetraethyl Urea, $\mathrm{CO}{<}\begin{matrix}\mathrm{N(C_2H_5)_2}\\\mathrm{N(C_2H_5)_2}\end{matrix}$, boils at 210–215°, and has an odor resembling that of peppermint.

Allyl Urea, $\mathrm{CO}{<}\begin{matrix}\mathrm{NH.C_3H_5}\\\mathrm{NH_2}\end{matrix}$, melts at 85°, and is converted by hydrogen bromide into *propylene-ψ-urea* (p. 404),



$\begin{matrix}\mathrm{CH_3.CH{-}O}\\\mathrm{CH_2{-}NH}\end{matrix}{>}\mathrm{C:NH}$ (B. 22, 2990).

Diallyl Urea, $\mathrm{CO}{<}\begin{matrix}\mathrm{NH.C_3H_5}\\\mathrm{NH.C_3H_5}\end{matrix}$, *Sinapoline*, is formed when allyl isocyanic ester is heated with water or by heating mustard oil with water and lead oxide. Diallyl thio-urea is first formed, but the lead oxide desulphurizes it (p. 425). Diallyl urea melts at 100°.

Ureo-ethanol, $\mathrm{HO.CH_2.CH_2.NH.CO.NH_2}$, melting at 95°, is obtained from oxyethylamine isocyanate or 2-amino-ethanol (B. 28, R. 1010).

Nitroso-ureas are formed when nitrites act upon the nitrates or sulphates of ureas which contain an alkyl group in the amido group:

Nitroso-methyl Urea, $\mathrm{NH_2.CO.N(NO)CH_3}$. *Nitroso-a-diethyl Urea*, $\mathrm{NH(C_2H_5)CON(NO)C_2H_5}$, melting at 5°, is a yellow oil at the ordinary temperature. The reduction of these compounds gives rise to the *semi-carbazides* or *hydrazine ureas*, which yield *alkyl hydrazines* (p. 171) when they are decomposed.

Nitro-urea, $\mathrm{NO_2.NH.CO.NH_2}$, is produced when urea nitrate is introduced into concentrated sulphuric acid. It forms a white, crystalline powder when recrystallized from water. This melts at higher temperatures with decomposition. It is a strong acid; its alkali salts are neutral in reaction, and expel acetic acid from acetates (A. 288, 281).

Nitro-ethyl Urea, $\mathrm{NO_2.NH.CO.NH.C_2H_5}$, melts at 130–131°.

Cyclic Alkylen Urea Derivatives.

The ureas and aldehydes combine at the ordinary temperature, with the exit of water, and yield the following compounds:

Methylene Urea, $CO<\begin{matrix}NH\\NH\end{matrix}>CH_2$, consists of white, granular crystals (B. **29,** 2751).

Ethidene Urea, $CO<\begin{matrix}NH\\NH\end{matrix}>CH.CH_3$, melts at 154°.

Ethylene Urea, $CO<\begin{matrix}NHCH_2\\NHCH_2\end{matrix}$, isomeric with ethidene urea, is produced on heating ethyl carbonate to 180°, together with ethylene-diamine. Needles, melting at 131°.

Dinitro-ethylene Urea, $CO<\begin{matrix}N.(NO_2).CH_2\\ \quad\quad\quad\quad | \\N.(NO_2).CH_2\end{matrix}$.

Trimethylene Urea, $CO<\begin{matrix}NH.CH_2\\NH.CH_2\end{matrix}>CH_2$, melts at 260° (A. **232,** 224).

Ethylene Diurea, $\begin{matrix}CO<\begin{matrix}NH_2\\NH\end{matrix}\\CO<\begin{matrix}NH\\NH_2\end{matrix}\end{matrix}>C_2H_4$, is produced upon heating ethylene diamine hydrochloride with silver cyanate. It melts at 192° with decomposition.

Very little is known relative to the action of urea upon *dialdehydes, aldehyde-ketones,* and *diketones: Acetylene Diurea,* Glycoluril, $CO<\begin{matrix}NH.CH.NH\\ | \\NH.CH.NH\end{matrix}>CO(?)$, is obtained from glyoxal and urea, as well as by the reduction of allantoïn (B. **19,** 2477).

Nitric acid converts it into *Dinitroglycoluril,* Acetylene-dinitro-diureïne, $CO<\begin{matrix}NH.CH.N(NO_2)\\ | \\NH.CH.N(NO_2)\end{matrix}>CO$, decomposes at 217°, and when boiled with water passes into *glycolureïne,* $CO<\begin{matrix}NH.CH.OH\\ | \\NH.CH.OH\end{matrix}$, isomeric with hydantoïc acid. Consult B. **26,** R. **291,** for the action of urea upon *acetyl acetone.*

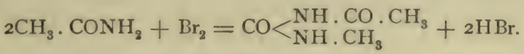
DERIVATIVES OF UREA WITH ACID RADICALS, OR UREÏDES.

The urea derivatives of the monobasic acids are obtained in the action of acid chlorides or acid anhydrides upon urea. By this procedure, however, it is possible to introduce but one radical. The compounds are solids; they decompose when heat is applied to them, and do not form salts with acids. Alkalies cause them to separate into their components.

Formyl Urea, $NH_2.CO.NH.CHO$, melts at 167° (B. **29,** 2046).

Acetyl Urea, $CO<\begin{matrix}NH.C_2H_3O\\NH_2\end{matrix}$, is not very soluble in cold water and alcohol. It forms long, silky needles, which melt at 214° (A. **229,** 30). Consult B. **28,** R. 63, for the metal derivatives of formyl and acetyl urea. Heat breaks it up into acetamide and isocyanuric acid. *Chloracetyl urea,* $H_2NCO.NH.CO.CH_2Cl$, decomposes about 160°. *Bromacetyl urea,* $NH_2CO.NH.CO.CH_2Br$, dissolves with difficulty in water. When heated with ammonia it changes to hydantoïn.

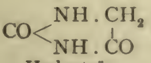
Methyl Acetyl Urea, $CO<\begin{matrix}NH.C_2H_3O\\NH.CH_3\end{matrix}$, is obtained from methyl urea upon digesting it with acetic anhydride, and by the action of bromine and potassium hydroxide upon acetamide (p. 163). It melts at 180°.



$$2CH_3.CONH_2 + Br_2 = CO<\begin{matrix}NH.CO.CH_3\\NH.CH_3\end{matrix} + 2HBr.$$

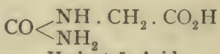
Diacetyl Urea, $CO<\begin{matrix}NH.C_2H_3O\\NH.C_2H_3O\end{matrix}$, results when $COCl_2$ acts on acetamide, and sublimes in needles without decomposition.

Ureïdes of Oxyacids.—Open and closed chain and ring-shaped or cyclic ureïdes are known. This is especially true of α-oxyacids, like lactic acid and α-oxyisobutyric acid. As the open-chain ureïdes are obtained from the closed-chain members by severing a lactam-union by means of alkalies or alkaline earths, therefore the former will be treated after concluding the cyclic ureïdes, *e. g.:*



$$CO<\begin{matrix}NH.CH_2\\ \quad | \\NH.CO\end{matrix}$$

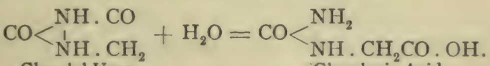
Hydantoïn,
Closed-chain Ureïde
of Glycollic Acid



$$CO<\begin{matrix}NH.CH_2.CO_2H\\NH_2\end{matrix}$$

Hydantoïc Acid,
Open-chain Ureïde
of Glycollic Acid.

Glycolyl Urea, $C_3H_4N_2O_2$, **Hydantoin,** may be obtained (1) from two very important oxidation products of uric acid—allantoïn and alloxanic acid—by heating them with hydriodic acid; synthetically (2) by heating bromacetyl urea with alcoholic ammonia, when hydrogen bromide is split off, and (3) by the action of urea upon dioxytartaric acid (A. **254**, 258). It melts at 216°. When boiled with baryta water, it passes into glycoluric or hydantoïc acid:



$$CO<\begin{matrix}NH.CO\\ | \quad\\NH.CH_2\end{matrix} + H_2O = CO<\begin{matrix}NH_2\\NH.CH_2CO.OH.\end{matrix}$$

Glycolyl Urea Glycoluric Acid.

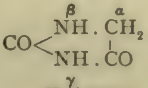
Nitrohydantoïn, $C_3H_3(NO_2)N_2O_2$, is produced when very strong nitric acid acts upon hydantoïn. It melts at 170°. When boiled with water it gives off CO_2 and passes into nitro-amido-acetamide (B. **22**, R. 58).

Glycoluric Acid, $C_3H_6N_2O_3$, **Hydantoïc Acid,** was originally obtained from uric acid derivatives (allantoïn, glyco-uril, hydantoïn), but may be synthesized by heating urea with glycocoll to 120°, or by digesting glycocoll sulphate with potassium isocyanate, analogous to urea.

Hydantoïc acid is very soluble in hot water and alcohol. When heated with hydriodic acid it yields CO_2, NH_3 and glycocoll.

Taurocarbamic Acid (see taurine, p. 311).

Hydantoïn Homologues.—The same succession of carbon and nitrogen atoms as was noticed in the hydantoïn occurs in the glyoxalines or imidazoles (p. 321). However, the hydantoïn ring is less stable than the glyoxaline ring. On replacing the hydrogen atoms of the CH_2- and the two NH-groups, the alkylic hydantoïns are obtained. They are known as α-, β- and γ-derivatives, and are represented as follows:



$$CO<\begin{matrix}\overset{\beta}{NH}.\overset{\alpha}{CH_2}\\ \quad | \\\underset{\gamma}{NH}.CO\end{matrix}$$

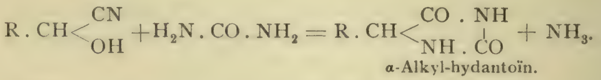
Hydantoïn.

The β-alkylic hydantoïns are formed when urea is fused together with mono-alkylic glycocolls. Water and ammonia are set free.

β-**Methyl-hydantoïn,** $C_3H_3(CH_3)N_2O_2$, was first obtained from creatinine, and is also formed when sarcosine (p. 355) is heated with urea; or by heating the sarcosine with cyanogen chloride (B. **15**, 2111). It melts at 157°.

β-**Ethyl-hydantoïn,** $C_3H_3(C_2H_5)N_2O_2$, crystallizes in rhombic plates which melt at 100° and sublime readily.

The γ-alkylic hydantoïns are produced by the action of alkalies and alkyl iodides upon α-hydantoïns (B. **25**, 327). The α-derivatives may be synthesized by heating the cyanhydrins of the aldehydes and ketones (p. 349) with urea (see α-phenylhydantoïn, and B. **21**, 2320):



$$R.CH{<}\begin{matrix}CN\\OH\end{matrix} + H_2N.CO.NH_2 = R.CH{<}\begin{matrix}CO\,.\,NH\\ \quad\mid\\ NH\,.\,CO\end{matrix} + NH_3.$$

α-Alkyl-hydantoïn.

α-**Lactyl Urea,** $C_4H_6N_2O_2$, α-**Methyl-hydantoïn.** It is formed from aldehyde ammonia along with alanine, if cyanide of potassium, containing potassium isocyanate, be used in its preparation. It melts at 140–145°. Boiled with baryta it absorbs water and forms α-*Lacturic Acid*, $CO{<}\begin{matrix}NH\,.\,CH(CH_3)\,.\,CO_2H\\NH_2\end{matrix}$, which melts at 155°.

Acetonyl Urea, $C_5H_8N_2O_2 = CO{<}\begin{matrix}NH - C(CH_3)_2\\ \qquad\mid\\ NH - CO\end{matrix}$, α-**Dimethyl-hydantoïn,** is obtained from acetone, prussic acid and cyanic acid (A. **164**, 264), as well as from pinacolyl sulphourea (p. 409). It melts at 175°. Boiling baryta water converts it into acetonyluric acid, $H_2N.CO.NH.C(CH_3)_2.CO_2H$, which fuses at 155–160°.

Both of the preceding bodies are ureïdes of α-oxyisobutyric acid.

Nitroacetonyl Urea, $\begin{matrix}(CH_3)_2C - N(NO_2)\\ \mid \qquad\qquad\\ CO - NH\qquad\quad\end{matrix}{>}CO$, melts at 140° (B. **22**, R. 58).

α-*Dialkylic Hydantoïns, e. g., α-Diethyl-hydantoïn,* $\begin{matrix}(C_2H_5)_2C - NH\\ \mid\qquad\\ CO - NH\end{matrix}{>}CO$, melting at 165°, can be prepared from cyanacetyl cyanide, by transposing it to diethylcyanacetyl cyanide, and then letting bromine and caustic potash act upon the latter. The non-tangible intermediate product, $(C_2H_5)_2C{<}\begin{matrix}CONH_2\\N:CO\end{matrix}$, rearranges itself into α-diethyl-hydantoïn (B. **29**, R. 517).

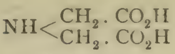
β-*Lactyl Urea,* $\begin{matrix}CH_2CO\,.\,NH\\ \mid\qquad\qquad\mid\\ CH_2.NH.CO\end{matrix}$, melting at 275° (B. **29**, R. 509), is analogously obtained from the unstable intermediate product, $\begin{matrix}CH_2\,.\,CO\,.\,NH_2\\ \mid\qquad\qquad\\ CH_2\,.\,N:CO\end{matrix}$, resulting from the action of bromine and caustic potash upon succinamide.

The ureïdes of glyoxylic acid, acetoacetic acid, oxalic acid, malonic acid, tartronic acid and mesoxalic acid will receive attention under the uric acid derivatives.

Di- and Tricarboxylamide Derivatives. *Ureïdes of Carbonic Acid.*—Free dicarbamidic or imidodicarbonic acid cannot exist. Some of its derivatives are rather remarkable. They sustain the same relation to carbamic acid that diglycolamidic acid bears to glycocoll. A derivative of tricarbamidic acid is known:

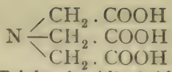
$NH_2 . CH_2 . CO_2H$

Amidoacetic Acid



$NH{<}\begin{matrix} CH_2 . CO_2H \\ CH_2 . CO_2H \end{matrix}$

Diglycolamidic Acid

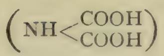


$N\begin{matrix} \diagup CH_2 . COOH \\ -CH_2 . COOH \\ \diagdown CH_2 . COOH \end{matrix}$

Triglycolamidic Acid

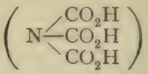
(NH_2COOH)

Carbamic Acid



$\left(NH{<}\begin{matrix} COOH \\ COOH \end{matrix}\right)$

Dicarbamidic Acid,
Imidodicarbonic Acid



$\left(N\begin{matrix} \diagup CO_2H \\ -CO_2H \\ \diagdown CO_2H \end{matrix}\right)$

Tricarbamidic Acid,
Nitrilotricarbonic Acid.

Dicarbamidic Ester, Imidodicarbonic Ester, $NH(CO_2C_2H_5)_2$, melts at 50° and boils at 215°. It results when $ClCO_2C_2H_5$ (B. **23**, 2785) acts upon sodium urethane (p. 394).

Allophanic Acid, $CO{<}\begin{matrix} NH_2 \\ NH . CO_2H \end{matrix}$, is not known in a free state. Its esters are formed (1) when chlorcarbonic esters (1 mol.) act upon urea (2 mols.) (B. **29**, R. 589); (2) by leading cyanic acid vapors into anhydrous alcohols. At first carbamic acid esters are produced; these combine with a second molecule of cyanic acid and yield allophanic esters (B. **22**, 1572):

$$CONH + NH_2 . CO_2 . C_2H_5 = NH_2CONHCO_2C_2H_5.$$

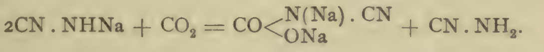
From carbamic esters or urethanes (3) by the action of urea chloride (B. **21**, 293), or (4) with thionyl chloride (B. **26**, 2172):

$$2NH_2CO_2C_2H_5 + SOCl_2 = NH_2CONH . CO_2C_2H_5 + HCl + SO_2 + C_2H_5Cl.$$

Ethyl Allophanic Ester, $NH_2 . CO . NH . CO_2 . C_2H_5$, melts at 190–191°. The *propyl ester* melts at 155°. The *amyl ester* melts at 162°.

The allophanic esters dissolve with difficulty in water, and, when heated, split up into alcohol, ammonia and cyanuric acid. The allophanates are obtained from them by means of the alkalies or baryta water. They show an alkaline reaction and are decomposed by carbonic acid. On attempting to free the acid by means of mineral acids, it at once breaks up into CO_2 and urea.

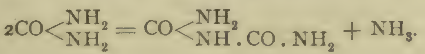
Cyanamido-carbonic Acid, $CO{<}\begin{matrix} NH . CN \\ OH \end{matrix}$, **Cyancarbamic Acid,** is the corresponding nitrile acid of allophanic acid. Its salts are formed by the addition of CO_2 to salts of cyanamide:



$$2CN . NHNa + CO_2 = CO{<}\begin{matrix} N(Na) . CN \\ ONa \end{matrix} + CN . NH_2.$$

The *esters* of this acid result by the action of alcoholic potash upon esters of *cyanamido-dicarbonic acid*, $CN . N{<}\begin{matrix} CO . C_2H_5 \\ CO . C_2H_5 \end{matrix}$.

Biuret, $CO{<}\begin{matrix} NH_2 \\ NH . CO . NH_2 \end{matrix} + H_2O$, *Allophanamide*, is formed on heating the allophanic esters with ammonia to 100°, or urea to 150–160°:



$$2CO{<}\begin{matrix} NH_2 \\ NH_2 \end{matrix} = CO{<}\begin{matrix} NH_2 \\ NH . CO . NH_2 \end{matrix} + NH_3.$$

It is readily soluble in alcohol and water, and crystallizes with 1 molecule of water, in the form of warts and needles. When anhydrous, biuret melts at 190°, and decomposes further into NH_3 and cyanuric acid. The aqueous solution, containing KOH, is colored a violet red by copper sulphate (B. **29**, 298; R. 589). Heated in a current of HCl, biuret decomposes into NH_3, CO_2, cyanuric acid, urea and guanidine.

Carbamin-cyanide, Cyan-urea, $NH_2 . CO . NH . CN$, the half nitrile of biuret, is formed, like urea, from guanidine, as well as from cyan-guanidine or dicyandiamide (p. 414), by action of baryta water, and when digested with mineral acids yields *biuret* (B. **8**, 708). See B. **25**, 820, for alkylic cyan-ureas.

Carbonyl Diurea, $C_3H_6N_4O_3$, is formed on heating urea with $COCl_2$ to 100°. It is a crystalline powder, not readily dissolved by water. Heat converts it into ammonia and cyanuric acid (p. 419) (B. **29**, R. 589).

Cyanamidodicarbonic Ester, $CN . N(CO_2C_2H_5)_2$, a derivative of amidotricarbonic acid, $N(CO_2H)_3$, not capable of existing, is formed when chlorcarbonic esters act upon sodium cyanamide (J. pr. Ch. [2] **16**, 146).

Derivatives of Imidocarbonic Acid.—The pseudo-forms, imidocarbonic acid and pseudo-urea, correspond to carbamic acid and urea:

$NH_2 . COOH$	$NH : C(OH)_2$	$CO(NH_2)_2$	$NH : C<{NH_2 \atop OH}$
Carbamic Acid	**Imidocarbonic Acid**	**Urea**	**ψ-Urea.**

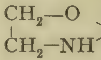
These modifications are not known in a free state, but many derivatives may be referred to them.

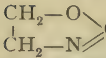
Imidocarbonic Ester, $HN : C(O . C_2H_5)_2$, boiling at 62° (36 mm.), is produced by reducing chlorimidocarbonic ester (B. **19**, 862, 2650) and from di-imido-oxalic ester (p. 438) by the action of alcoholic sodium ethylate (B. **28**, R. 760). At 200° it breaks down into alcohol and cyanuric ether (B. **28**, 2466).

Ethyl Imidochlorcarbonic Ester, $C_2H_5N : CCl(OC_2H_5)$, boiling at 126°, is formed by the union of ethyl isocyanide (p. 237) with ethyl hypochlorite (B. **28**, R. 760).

Chlorimido-carbonic Ethyl Ester, $ClN : C(O . C_2H_5)_2$, melting at 39°, and the *methyl ester*, melting at 20°, are produced in the action of esters of hypochlorous acid (p. 147) upon a concentrated potassium cyanide solution. They are solids, with a peculiar penetrating odor, and distil with decomposition. Alkalies have little effect upon them, while acids break them up quite easily, forming ammonia, esters of carbonic acid and nitrogen chloride.

Bromimido-carbonic Ethyl Ester, $BrN : C(OC_2H_5)_2$, melting at 43°, results when bromine acts upon imidocarbonic ester (B. **28**, 2470).





Derivatives of ψ-Urea.—Ethylene-pseudo-Urea, $\begin{array}{l} CH_2{-}O \\ | \\ CH_2{-}NH \end{array}\!\!>C : NH$, or $\begin{array}{l} CH_2{-}O \\ | \\ CH_2{-}N \end{array}\!\!\gg C . NH_2$, is produced by the action of brom-ethylamine hydrobromide upon potassium cyanate. It is a basic oil, which solidifies with difficulty.

Propylene-ψ-Urea, $C_3H_6 : CON_2H_2$, results from HBr-propylamine and potassium cyanate, as well as from allyl urea, by a molecular rearrangement induced by hydrobromic acid (B. **22**, 2991).

Diamide- or Hydrazine, and Di-imide Derivatives of Carbonic Acid.—*Hydrazine Carbonic Ester*, $NH_2 . NH . CO_2 . C_2H_5$, is formed by reducing nitro-urethane with zinc and acetic acid. Its *benzal derivative*, $C_6H_5 . CH : N . NH . CO_2 . C_2H_5$, melts at 135° (A. **288**, 293).

Semicarbazide, Carbamic Hydrazide, $NH_2 . CO . NH . NH_2$, melting at 96°, is formed (1) by heating urea and hydrazine hydrate to 100° (J. pr. Ch. [2], **52**, 465); (2) from hydrazine sulphate and potassium cyanide; (3) from amido-guanidine (B. **27**, 31, 56); (4) from nitro-urea (A. **288**, 311). With benzaldehyde it yields *benzal-semicarbazide*, $NH_2 . CO . NHN = CH . C_6H_5$, melting at 214°. *Acetone Semicarbazone*, $NH_2 . CO . NH . N : C(CH_3)_2$, melting at 187°, passes into bisdimethylazimethylene (p. 220) (B. **29**, 611).

Acetoacetic Ester Carbazone, $NH_2 . CO . NH . N : C(CH_3) . CH_2 . CO_2C_2H_5$, melting at 129° (A. **283**, 18), readily passes into a lactazam. Semicarbazide condenses with benzil to 1.2-diphenyl oxytriazine. Semicarbazide is a reagent for aldehydes and ketones.

Carbohydrazide, $NH_2 . NH . CO . NH . NH_2$, melting at 152–153°, is obtained from carbonic ester and hydrazine hydrate on heating to 100° (J. pr. Ch. [2] **52**, 469). *Dibenzal Carbohydrazide*, $CO(NH . N = CH . C_6H_5)_2$, melts at 198°.

Hydrazo-dicarbonic Ester, Hydrazi-carbonic Ester, $C_2H_5O . CO . NH . NH . CO . O . C_2H_5$, melting at 130°, boils with decomposition about 250°, and is prepared from hydrazine and $Cl . CO_2C_2H_5$ (B. **27**, 773; J. pr. Ch. [2] **52**, 476).

Hydrazo-dicarbonamide, Hydrazo-formamide, $NH_2 . CONH . NH . CONH_2$, melts with decomposition at 244–245°. It is obtained from potassium cyanate and salts of diamide or hydrazine: $NH_2 . NH_2$. It also results upon heating semicarbazide (B. **27**, 57), and from *Azodicarbonamide*, $NH_2 . CON = N . CONH_2$, by reduction. It yields the latter upon oxidation (A. **271**, 127; B. **26**, 405).

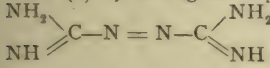
Cyclic Hydrazine Derivatives of Urea.—Urazole, Hydrazo-dicarbonimide, $\left.\begin{array}{l}NH . CO\\ | \\ NH . CO\end{array}\right>NH$, melting at 244°, forms on heating hydrazo-dicarbonamide to 200° (A. **283**, 16), or from urea and hydrazine sulphate heated to 120° (B. **27**, 409). See also triazole. It is a strong, monobasic acid.

Methylene Carbohydrazide, $CO\left<\begin{array}{l}NH . N\\NH . NH\end{array}\right>CH$, melting at 181°, is produced on heating carbohydrazide with orthoformic ester to 100° (J. pr. Ch. [2], **52**, 475).

Diurea, Bishydrazine Carbonyl, $CO\left<\begin{array}{l}NH . NH\\NH . NH\end{array}\right>CO$, melting at 270°, is formed from hydrazine carbonic ester and hydrazine hydrate at 100° (B. **27**, 2684; J. pr. Ch. [2], **52**, 482).

Azodicarbonic Acid, *Azoformic Acid*, $CO_2H . N = N . CO_2H$. Its potassium salt explodes when heated above 100°. It consists of small yellow needles. It is formed when azodicarbonamide is boiled with concentrated caustic potash. It readily decomposes in aqueous solution, giving off CO_2, potassium carbonate, diamide and nitrogen. The isolation of the unknown *di-imide* $NH = NH$, present in it, has not yet proved successful. The *diethyl ester*, boiling at 106° (13 mm.) is an orange-yellow-colored oil, and is formed when nitric acid acts upon the hydrazoester.

Azodicarbonamide, Azoformamide, $NH_2CON = NCONH_2$, is an orange-red-colored powder. It is produced (1) on oxidizing hydrazodicarbonamide with chromic acid; (2) by boiling the aqueous solution of the nitrate of *azodicarbonamidine*,



$$\begin{array}{l}NH_2\\NH\end{array}\!\!>C—N = N—C\!<\!\!\begin{array}{l}NH_2\\NH\end{array}$$

(p. 415).

Potassium Azimethane Disulphonate, $\begin{array}{l}N : C(SO_3K)_2\\ | \\ N : C(SO_3K)_2\end{array} . 2H_2O$, is formed on boiling *potassium diazomethane-disulphonate*, $\left.\begin{array}{l}N\\ \| \\ N\end{array}\right>C(SO_3K)_2$, in xylene solution. Orange-yellow-colored needles, which result when a solution of potassium nitrite acts upon primary potassium amino-methane disulphonate, $NH_2 . CH(SO_3K)_2$—the addition product of prussic acid and monopotassium sulphite (B. **29**, 2161).

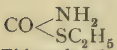
Hydroxylamine Derivatives of Carbonic Acid.—Oxyurethane, HO . NH . -

$CO_2 . C_2H_5$, or $HON:C<^{O.C_2H_5}_{OH}$, is a colorless liquid. It is produced when an hydroxylamine solution acts upon chlorcarbonic ester (B. **27**, 1254).

Hydroxyl Urea, $NH_2 . CO . NH . OH$, melting at 128–130°, dissolves readily in water and alcohol, but with difficulty in ether. It is obtained from hydroxylamine nitrate and potassium isocyanate (A. **182**, 214).

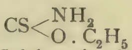
SULPHUR-CONTAINING DERIVATIVES OF CARBAMIC ACID AND OF UREA.

The following compounds correspond to urethane and urea:



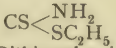
$CO<^{NH_2}_{SC_2H_5}$

Thiocarbamic Ester



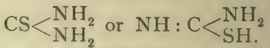
$CS<^{NH_2}_{O.C_2H_5}$

Sulphocarbamic Ester



$CS<^{NH_2}_{SC_2H_5}$

Dithiocarbamic Ester



$CS<^{NH_2}_{NH_2}$ or $NH:C<^{NH_2}_{SH.}$

Sulphourea.

Many reactions of sulphourea indicate that its constitution is probably best expressed by a formula analogous to one of the non-existing pseudo forms of urea.

Imido-thiocarbonic Acid, $NH:C<^{OH}_{SH}$, is an hypothetical acid. Its derivatives are all of the aromatic series (see phenyl-isothio-urethane), unless the alkylic derivatives of thiocarbamic acid are to be referred to this pseudo-form.

Thiocarbamic Acid, Carbamine Thiol Acid, $CO<^{NH_2}_{SH}$, is not known in the free state. Its *ammonium salt* is prepared by leading COS into alcoholic ammonia (A. **285**, 173). It is a colorless, crystalline mass, which acquires a yellow color on exposure to the air, owing to the formation of ammonium sulphide. When heated to 130° it breaks up into hydrogen sulphide and urea.

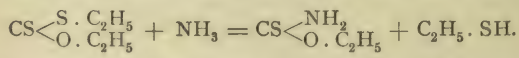
The *methyl ester*, $NH_2 . CO . S . CH_3$, melting at 95–98°, and the *ethyl ester*, melting at 108°, are obtained by conducting hydrochloric acid gas into a solution of CNSK (or of alkyl sulphocyanates—B. **19**, 1083) in alcohols (together with esters of sulphocarbamic acid—J. pr. Ch., [2] **16**, 358); and by the action of ammonia upon the dithiocarbonic esters and chlorthioformic esters.

These are crystalline compounds which dissolve with difficulty in water.

Ethyl Ethosulphocarbamic Ester, $C_2H_5 . NH . CO\ S . C_2H_5$, boils at 204–208°. It results from the union of ethyl isocyanate with ethyl mercaptan.

Sulphocarbamic Acid, Xanthogenamic Acid, NH_2CSOH, is known in its alkyl compounds.

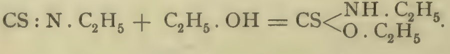
The esters of **sulphocarbamic acid**—thiourethanes, the xanthogenamides—are formed when alcoholic ammonia acts upon the xanthic esters (p. 391):



$$CS<^{S.C_2H_5}_{O.C_2H_5} + NH_3 = CS<^{NH_2}_{O.C_2H_5} + C_2H_5 . SH.$$

The *ethyl ester* of sulphocarbamic acid is slightly soluble in water and melts at 38°. The *methyl ester* melts at 43°. It is slightly soluble in water. Both esters decompose into mercaptans, cyanic acid and cyanuric acid on heating. Alcoholic alkalies decompose them into alcohols and thiocyanates.

The esters of *alkylic* sulphocarbamic acids are obtained when the mustard oils are heated to 110° with anhydrous alcohols:

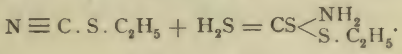


$$CS:N . C_2H_5 + C_2H_5 . OH = CS<^{NH . C_2H_5}_{O . C_2H_5}.$$

They are liquids with an odor like that of leeks, boil without decomposition and break up into alcohols, CO_2, H_2S and alkylamines, when acted upon with alkalies or acids *Ethyl Sulphocarbamic Ethyl Ester*, $C_2H_5 . NH . CS . O . C_2H_5$, boils at 204°–208°. *Allyl Sulphocarbamic Ethyl Ester*, $C_3H_5 . NH . CS . O . C_2H_5$, from allyl mustard oil, boils at 210°–215°.

Dithiocarbamic Acid, $NH_2 . CS . SH$ or $NH = C(SH)_2$, is obtained as a red oil upon decomposing its ammonium salt with dilute sulphuric acid. It readily breaks down into sulphocyanic acid, $CN . SH$, and hydrogen sulphide. Water decomposes it into cyanic acid and $2H_2S$. Its *ammonium salt*, $NH_2 . CS . SNH_4$, is formed when alcoholic ammonia acts upon carbon disulphide. It consists of yellow needles or prisms. It yields *mercaptothiazoles* with α-halogen ketones (B. **26**, R. 604).

The **dithiourethanes** are the esters of the above acid. They arise when the thiocyanic esters are heated with H_2S (compare phenyl dithiocarbamic acid):

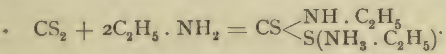


$$N \equiv C . S . C_2H_5 + H_2S = CS<^{NH_2}_{S . C_2H_5}.$$

They are crystalline compounds, soluble in alcohol and ether, and are decomposed into ammonium thiocyanate and mercaptans, when treated with alcoholic ammonia.

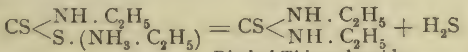
The *ethyl ester* melts at 41–42° and the *propyl ester* at 97°.

Alkyl-dithiocarbamic Acids.—The amine salts of these compounds are obtained on heating CS_2 with alcoholic solutions of the primary and secondary amines:



$$CS_2 + 2C_2H_5 . NH_2 = CS<^{NH . C_2H_5}_{S(NH_3 . C_2H_5)}.$$

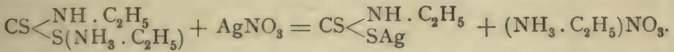
When the amine salts of ethyl-dithiocarbamic acid are heated to 110°, dialkylic thio-ureas are produced (p. 408):



$$CS<^{NH . C_2H_5}_{S . (NH_3 . C_2H_5)} = CS<^{NH . C_2H_5}_{NH . C_2H_5} + H_2S$$

Diethyl Thiocarbamide.

If the aqueous solution of the salts obtained from the primary amines be digested with metallic salts, *e.g.*, $AgNO_3$, $FeCl_3$ or $HgCl_2$, salts of ethyl-dithiocarbamic acid are precipitated:



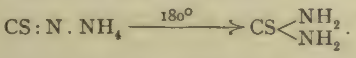
$$CS<^{NH . C_2H_5}_{S(NH_3 . C_2H_5)} + AgNO_3 = CS<^{NH . C_2H_5}_{SAg} + (NH_3 . C_2H_5)NO_3.$$

These yield the mustard oils, or isothiocyanic esters, when boiled with water (p. 423).

The salts obtained from the secondary amines do not yield mustard oils (B. **8**, 107).

Carbothialdine, $NH_2CSSN(CH . CH_3)_2$, is produced by heating ammonium dithiocarbamate together with aldehyde. It is also produced on mixing CS_2 with alcoholic aldehyde-ammonia (B. **11**, 1383). It consists of large, shining crystals, and when boiled with acids decomposes into ammonia, carbon disulphide and aldehyde.

Thiourea, Sulphocarbamide, $CS<^{NH_2}_{NH_2}$, or $NH : C<^{NH_2}_{SH}$, melting at 172°, is obtained (as first observed by Reynolds in 1869—A. **150**, 224) by heating ammonium thiocyanate to 170–180° (A. **179**, 113), when a transposition analogous to that occurring in the formation of urea takes place (p. 397). This synthesis, however, does not proceed with ease, and is never complete, because at 160–170° sulphourea is again changed to ammonium sulphocyanate:



$$CS : N . NH_4 \xrightarrow{180°} CS<^{NH_2}_{NH_2}.$$

Sulphourea is also produced by the action of hydrogen sulphide (in presence of a little ammonia) or ammonium thiocyanate upon cyanamide (B. **8**, 26):

$$\mathrm{CN.NH_2 + SH_2 = CS}{<}\begin{matrix}\mathrm{NH_2}\\\mathrm{NH_2}\end{matrix}.$$

Sulphocarbamide crystallizes in thick, rhombic prisms, which dissolve easily in water and alcohol, but with difficulty in ether; they possess a bitter taste and have a neutral reaction.

Transpositions: (1) When sulphocarbamide is heated with water to 140° it again becomes ammonium thiocyanate. (2) If boiled with alkalies, hydrochloric acid or sulphuric acid, it decomposes according to the equation:

$$\mathrm{CSN_2H_4 + 2H_2O = CO_2 + 2NH_3 + H_2S.}$$

(3) Silver, mercury, or lead oxide and water will convert it, at ordinary temperatures, into cyanamide, CN_2H_2; and on boiling into dicyandiamide (p. 414). (4) $KMnO_4$ converts it, in cold aqueous solution, into urea. (5) In nitric acid solution, or by means of H_2O_2 in oxalic acid solution, salts of a disulphide, $NH_2 . C = (NH)S - S(NH) = C . NH_2$, not known in a free state, are produced (B. **24**, R. 71). See B. **25**, R. 676, upon the condensation of thiourea with aldehyde ammonias. Sulphourea condenses with α-chloraldehydes and α-chlorketones to *amidothioazoles*. It yields *aromatic glyoxaline* derivatives when heated with benzoïn.

Constitution.—The behavior of thiourea when oxidized in acid solution and certain other reactions rather support the formula $\mathrm{NH:C}{<}\begin{matrix}\mathrm{NH_2}\\\mathrm{SH}\end{matrix}$ instead of the diamide formula (compare J. pr. Ch. [2] **47**, 135). Possibly free thiourea possesses the symmetrical formula, while its salts are derived from the *pseudo-form* $\mathrm{NH:C}{<}\begin{matrix}\mathrm{NH_2}\\\mathrm{SH}\end{matrix}$ (p. 54).

Thiourea combines with 1 equivalent of acid to form salts. The *nitrate*, $CSN_2H_4 . HNO_3$, occurs in large crystals. Auric chloride and platinic chloride throw down red-colored double chlorides from the concentrated solution. Silver nitrate precipitates $CSN_2H_4NO_3Ag$ (B. **24**, 3956; B. **25**, R. 583). For the constitution of these metallic salts see B. **17**, 297.

Alkyl Sulphocarbamides, in which the alkyl groups are linked to nitrogen, are produced—

(1) On heating the mustard oils with primary and secondary amine bases (A. W. Hofmann, B. **1**, 27):

$$\mathrm{CS:N.C_2H_5 + NH_3 = CS}{<}\begin{matrix}\mathrm{NH.C_2H_5}\\\mathrm{NH_2}\end{matrix}$$

Ethyl Sulphocarbamide

$$\mathrm{NH_2.C_2H_5 + CS:N.C_2H_5 = NHC_2H_5CSNHC_2H_5}$$

Sym. Diethyl Sulphourea

$$\mathrm{NH(C_2H_5)_2 + CS:N.C_2H_5 = N(C_2H_5)_2CSNHC_2H_5}$$

Triethyl Sulphourea.

(2) By heating the amide salts of the alkyl dithiocarbamic acids (B. **1**, 25) (p. 407):

$$\mathrm{CS}{<}\begin{matrix}\mathrm{NH.C_2H_5}\\\mathrm{S(NH_3.C_2H_5)}\end{matrix} = \mathrm{CS}{<}\begin{matrix}\mathrm{NH.C_2H_5}\\\mathrm{NH.C_2H_5}\end{matrix} + \mathrm{H_2S.}$$

Ethyl Sulphocarbamide, $CS<\begin{matrix}NH\,.\,C_2H_5\\NH_2\end{matrix}$, melting at 113°, dissolves readily in water and alcohol.

Sym. **Diethyl Sulphocarbamide,** $CS<\begin{matrix}NH\,.\,C_2H_5\\NH\,.\,C_2H_5\end{matrix}$, melts at 77°. Unsym. *Diethylthiourea* melts at 169°. *Triethylthiourea* melts at 26° and boils at 205°. *Monomethylthiourea* melts at 119°. Sym. *Dimethylthiourea* melts at 61° (B. **24,** 2729; **28,** R. 424). Unsym. *Dimethylthiourea,* $NH_2CSN(CH_3)_2$, melts at 159° (B. **26,** 2505). *Propylthiourea,* see B. **23,** 286; **26,** R. 87.

Allyl Sulphocarbamide, $CS<\begin{matrix}NH\,.\,C_3H_5\\NH_2\end{matrix}$, *Thiosinamine,* is formed by the union of allyl mustard oil with ammonia (p. 425).

It melts at 74°. It is readily soluble in water, alcohol and ether. Allyl cyanamide and triallyl-melamine are produced on boiling with mercuric oxide or lead hydroxide (p. 427). Hydrogen bromide changes it to propylene-pseudothiourea (comp. B. **29,** R. 684).

Transformations of the Alkyl Sulphoureas.

(1) The sulphocarbamides regenerate amines and mustard oils by distillation with P_2O_5, or when heated in HCl-gas:

$$CS<\begin{matrix}NH(C_2H_5)\\NH(C_2H_5)\end{matrix} = CS:N\,.\,C_2H_5 + NH_2\,.\,C_2H_5.$$

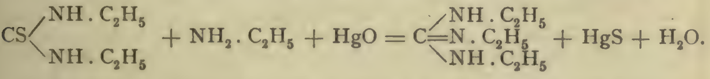
(2) The sulphur in the alkylic sulphocarbamides may be replaced by oxygen if these compounds are boiled with water and mercuric oxide or lead oxide. Those that contain two alkyl groups yield the corresponding ureas:

$$CS<\begin{matrix}NH\,.\,C_2H_5\\NH\,.\,C_2H_5\end{matrix} + HgO = CO<\begin{matrix}NH\,.\,C_2H_5\\NH\,.\,C_2H_5\end{matrix} + HgS;$$

whereas the mono-derivatives pass into alkylic cyanamides (and melamines) after parting with hydrogen sulphide (pp. 393, 394):

$$CS<\begin{matrix}NH\,.\,C_2H_5\\NH_2\end{matrix} = N\,{\vdots}\,C\,.\,NH\,.\,C_2H_5 + SH_2.$$

(3) On digesting the dialkylic sulphocarbamides with mercuric oxide and amines, oxygen is exchanged for the imid-group and guanidine derivatives appear (p. 411):



$$CS\begin{matrix}\diagup NH\,.\,C_2H_5\\ \\ \diagdown NH\,.\,C_2H_5\end{matrix} + NH_2\,.\,C_2H_5 + HgO = C\begin{matrix}\diagup NH\,.\,C_2H_5\\ =N\,.\,C_2H_5\\ \diagdown NH\,.\,C_2H_5\end{matrix} + HgS + H_2O.$$

Consult B. **23,** 271, upon the constitution of the dialkylic sulphocarbamides.

Ethylene Sulphocarbamide, $CS<\begin{matrix}NH\\NH\end{matrix}>C_2H_4$, is obtained from ethylene-diamine and carbon disulphide (B. **5,** 242). It melts at 195°.

Pinacolyl Sulphocarbamide, Tetramethyl-ethylene-sulphocarbamide, Carbothiacetonine, $CS[NHC(CH_3)_2]_2$, melts at 240–243°, and is formed by the action of ammonia upon carbon disulphide and acetone (B. **29,** R. 669).

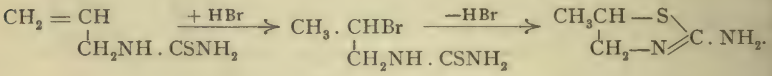
Derivatives of Pseudosulphocarbamide.—In the preceding derivatives (immaterial whether they are derived from the sym. or unsym. sulphocarbamide formula) the alkyl groups were in all cases joined to nitrogen, whereas the compounds about to be described must be considered as derivatives of pseudosulphocarbamide.

The *alkylic pseudosulphocarbamides* result upon the addition of alkyl iodides to the thioureas. The alkyl groups contained in them are united with sulphur because, when they are acted upon with ammonia, they are changed to guanidines and mercaptans (B. **11,** 492; **23,** 2195).

Alkylen Derivatives of Pseudosulphourea.

Ethylene-pseudothiourea, $NH.C\langle\begin{array}{l}S-CH_2\\ NH.CH_2\end{array}$ or, more probably, $NH_2C\langle\begin{array}{l}S-CH_2\\ N-CH_2\end{array}$, is obtained from HBr-ethyleneamine and potassium thiocyanate. It is a base with strong basic properties. Its salts crystallize well. It melts at 85° (B. **22**, 1141, 2984; **24**, 260).

Propylene-pseudothiourea, $C_3H_6:CSN_2H_2$, from brompropylamine and potassium thiocyanate, is perfectly similar. It also results from allyl thiourea by action of hydrobromic acid:



$$\begin{array}{l}CH_2=CH\\ \quad CH_2NH.CSNH_2\end{array}\xrightarrow{+HBr}\begin{array}{l}CH_3.CHBr\\ \quad CH_2NH.CSNH_2\end{array}\xrightarrow{-HBr}\begin{array}{l}CH_3CH-S\\ CH_2-N\end{array}\rangle C.NH_2.$$

Acetyl Pseudosulphocarbamide, $HN=C\langle\begin{array}{l}NH_2\\ S.C_2H_3O,\end{array}$ is obtained from thiourea by heating it with acetic anhydride; also from cyanamide (carbodiïmide, p. 426) and thioacetic acid. This second method argues for the compound being a derivative of pseudosulphocarbamide. It melts at 165°.

Pseudothio-, or -sulpho-hydantoïn, $HN:C\langle\begin{array}{l}NH.CO\\ S-CH_2\end{array}$, is obtained when chloracetic acid (A. **166**, 383) acts on sulphocarbamide, and was formerly thought to be the real thiohydantoïn, $CS\langle\begin{array}{l}NH.CO\\ NH.CH_2\end{array}$. However, its formation from cyanamide and thioglycollic acid and its decomposition, when boiled with baryta water, into thioglycollic acid and dicyandiamide prove that it is a pseudosulphocarbamide derivative, which contains the ring (p. 423) occurring in thiazole compounds (B. **12**, 1385, 1588).

Pseudosulphohydantoïn crystallizes from hot water in long needles, and decomposes near 200°.

Boiling acids convert it into *mustard-oil acetic acid*, $CO\langle\begin{array}{l}NH.CO\\ S-CH_2\end{array}$, with elimination of NH_3.

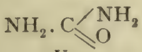
Hydrazine Derivatives of Thiocarbonic Acid.

Diammonium Dithiocarbazinate, $NH_2.NH.CSSNH_3.NH_2$, melting at 124°, is formed when hydrazine hydrate acts upon CS_2 (B. **29**, R. 233). *Hydrazodicarbonthiamide*, $NH_2CS.NH.NH.CS.NH_2$, melting at 214°, is formed on boiling a solution of hydrazine sulphate with ammonium sulphocyanide (B. **26**, 2877), with the simultaneous production of *Thiosemicarbazide*, $NH_2.NH.CS.NH_2$, melting at 181–183° (B. **28**, 948). *Methyl thiosemicarbazide*, $CH_3.NH.CS.NH.NH_2$, melting at 137°, and *Dimethyl thiosemicarbazide*, $CH_3.NH.CSNH.NHCH_3$, melting at 138°, are formed from methylene mustard oil, hydrazine and methyl hydrazine (B. **29**, 2920). *Hydrazodicarbon thioallylamide*, $C_3H_5NH.CSNH.NH.CSNHC_3H_5$ (B. **29**, 859). *Formyl methyl thiosemicarbazide*, $CH_3.NH.\begin{array}{l}NH-NH\\ C:S-CHO\end{array}$, melting at 167°, combines with acetyl chloride to *Methyl imidothiodiazoline*, $CH_3.NH.\begin{array}{l}NH-N\\ CS.-CH\end{array}$, melts at 245° (B. **27**, 622).

Dithiourazole, $\begin{array}{l}NH.CS\\ NH.CS\end{array}\rangle NH$, melts at about 245° with decomposition, and is formed on heating hydrazodicarbonthiamide with hydrochloric acid. The hydrochloride of imidothiourazole, $\begin{matrix}\text{NH . CS}\\ \text{NH . C(NH)}\end{matrix}\!\!>\!\text{NH}$, is produced at the same time (B. **28**, 949).

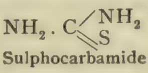
GUANIDINE AND ITS DERIVATIVES.

Guanidine is, upon the one hand, very closely related to orthocarbonic ester, urea and sulphocarbamide, and, upon the other, to cyanamide (p. 426). The carbonic acid derivatives just mentioned are united by a series of reactions. Guanidine belongs to the amidines, and may be regarded as the amidine of amidocarbonic acid:



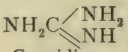
$$NH_2.C\begin{matrix}\diagup NH_2\\ \diagdown O\end{matrix}$$

Urea



$$NH_2.C\begin{matrix}\diagup NH_2\\ \diagdown S\end{matrix}$$

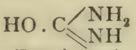
Sulphocarbamide



$$NH_2C\begin{matrix}\diagup NH_2\\ \diagdown NH\end{matrix}$$

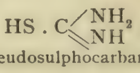
Guanidine.

The pseudo-forms of urea and thiourea—



$$HO.C\begin{matrix}\diagup NH_2\\ \diagdown NH\end{matrix}$$

(Pseudourea)

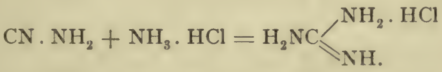


$$HS.C\begin{matrix}\diagup NH_2\\ \diagdown NH\end{matrix}$$

(Pseudosulphocarbamide).

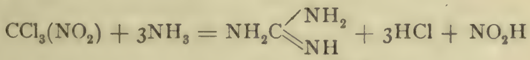
known in the form of various derivatives, are the amidines of carbonic and thiocarbonic acids.

Guanidine, $HN:C<\begin{matrix}NH_2\\ NH_2\end{matrix}$, was first obtained (A. Strecker, 1861) by the oxidation of guanine (a substance closely related to uric acid, and found in guano) with hydrochloric acid and potassium chlorate. It is found in certain seeds and in beet-juice (B. **29**, 2651). It is also important as the substance from which creatine is derived. It is formed synthetically (1) by heating cyanogen iodide and NH_3, and from cyanamide (p. 426) and ammonium chloride in alcoholic solution at 100°:

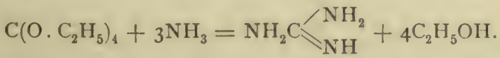


$$CN.NH_2 + NH_3.HCl = H_2NC\begin{matrix}\diagup NH_2.HCl\\ \diagdown NH.\end{matrix}$$

This is analogous to the formation of formamidine from HCN. (2) It is also produced by heating chloropicrin or (3) esters of orthocarbonic acid, with aqueous ammonia, to 150°:

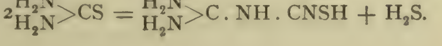


$$CCl_3(NO_2) + 3NH_3 = NH_2C\begin{matrix}\diagup NH_2\\ \diagdown NH\end{matrix} + 3HCl + NO_2H$$



$$C(O.C_2H_5)_4 + 3NH_3 = NH_2C\begin{matrix}\diagup NH_2\\ \diagdown NH\end{matrix} + 4C_2H_5OH.$$

(4) It is most readily prepared from the sulphocyanate, which is made by prolonged heating of ammonium sulphocyanate to 180-190°, and the further transposition of the thio-urea that forms at first (B. **7**, 92):



$$2\begin{matrix}H_2N\\ H_2N\end{matrix}\!>CS = \begin{matrix}H_2N\\ H_2N\end{matrix}\!>C.NH.CNSH + H_2S.$$

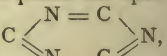
The crystals of guanidine are very soluble in water and alcohol, and deliquesce on exposure. Baryta water changes it to urea.

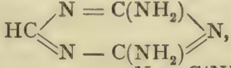
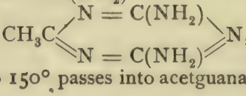
Salts.—It is a strong base, absorbing CO_2 from the air and yielding crystalline salts with 1 equivalent of the acids. The *nitrate*, $CN_3H_5 . HNO_3$, consists of large scales, which are sparingly soluble in water. The *HCl-salt*, $CN_3H_5 . HCl$, yields a platinum double salt, crystallizing in yellow needles. The *carbonate*, $(CN_3H_5)_2 . H_2CO_3$, consists of quadratic prisms, and reacts alkaline. The *sulphocyanate*, $CN_3H_5 . HSCN$, crystallizes in large leaflets, that melt at 118°.

The *alkyl guanidines* result (1) on heating cyanamide with the HCl-salts of the primary amines—*e g.*, **Methyl Guanidine**; (2) by boiling sym. dialkylic thio-ureas (p. 408) with mercuric oxide and ethylamine in alcoholic solution (B. **2**, 601): **Triethyl Guanidine.**

Vice versâ, the alkylic guanidines, when heated with CS_2, have their imid-group replaced by sulphur, with formation of thio-ureas.

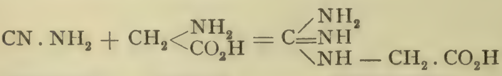
Guanidine also forms salts with the fatty acids. When these are heated to 220–230°, water and ammonia break off, and the **guanamines** result. These are peculiar heterocyclic bases (Nencki, B. **9**, 228). They are produced by the union of 1 molecule of acid and 2 molecules of guanidine.

Formoguanamine is also produced when chloroform and caustic potash act upon *biguanide* (p. 419) (B. **25**, 535). These bases contain the ring  assumed to be present in the cyanuric compounds.

Formoguanamine,  melts with decomposition at high temperatures. *Acetguanamine*,  melting at 265°, when heated with concentrated H_2SO_4 to 150° passes into acetguanamide; see acetylurethane.

Guaneides of the Oxyacids.—The guanidine derivatives corresponding to the ureïdes of glycollic acid, hydantoïc acid, and hydantoïn are known. Creatine and creatinine, important from a physiological standpoint, belong to this class.

Glycocyamine, guanidoacetic acid,  $NH = C<\begin{array}{l}NH_2\\ HCH_2CO_2H\end{array}$, is obtained by the direct union of glycocoll with cyanamide:

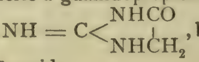


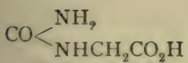
$$CN . NH_2 + CH_2<\begin{array}{l}NH_2\\ CO_2H\end{array} = C\begin{array}{l}\diagup NH_2\\ =NH\\ \diagdown NH - CH_2 . CO_2H\end{array}$$

Cyanamide Glycocoll Glycocyamine.

On mixing the aqueous solutions it separates after a time in granular crystals. It dissolves with difficulty in cold water and rather readily in hot water; while it is insoluble in alcohol and ether. It forms crystalline compounds with acids and bases.

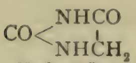
β-**Guanidopropionic Acid**, *Alacreatine*, $CN_3H_4 . CH_2 . CH_2 . CO_2H$, consists of crystals which decompose at 205°. Isomeric α-guanidopropionic acid melts at 180°.

Glycocyamidine, glycolyl guanidine,  bears the same relation to glycocyamine as hydantoïn to hydantoïc acid:



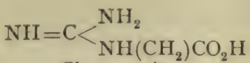
$CO<\begin{matrix}NH_2\\ NHCH_2CO_2H\end{matrix}$

Hydantoïc Acid



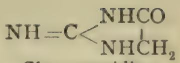
$CO<\begin{matrix}NHCO\\ NHCH_2\end{matrix}$

Hydantoïn



$NH{=}C<\begin{matrix}NH_2\\ NH(CH_2)CO_2H\end{matrix}$

Glycocyamine

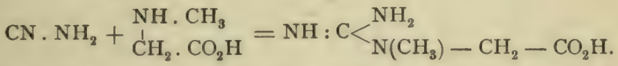


$NH{=}C<\begin{matrix}NHCO\\ NHCH_2\end{matrix}$

Glycocyamidine.

It is produced when glycocyamine hydrochloride is heated to 160°.

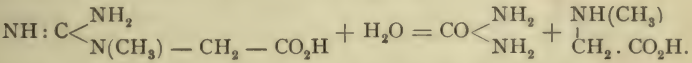
Creatine, methyl glycocyamine, methylguanidine acetic acid, $NH:C<\begin{matrix}NH_2\\ N(CH_3)CH_2CO_2H\end{matrix}$, was first discovered in 1834 by Chevreul in meat extract (*κρέας*, flesh). Liebig (1847) gave it a thorough investigation in his classic research entitled "Ueber die Bestandtheile der Flüssigkeiten des Fleisches" (A. **62**, 257). It is found especially in the juice of muscles. It may be artificially prepared (J. Volhard, 1869), like glycocyamine, by the union of sarcosine (methyl glycocoll) with cyanamide:



$$CN.NH_2 + \begin{matrix}NH.CH_3\\ |\\ CH_2.CO_2H\end{matrix} = NH:C<\begin{matrix}NH_2\\ N(CH_3)-CH_2-CO_2H.\end{matrix}$$

Creatine crystallizes with one molecule of water in glistening prisms. Heated to 100°, they sustain a loss of water. It reacts neutral, has a faintly bitter taste, and dissolves rather readily in boiling water; it dissolves with difficulty in alcohol, and yields crystalline salts with one equivalent of acid.

(1) When digested with acids, creatine loses water and becomes creatinine (see above), and (2) with baryta water it falls into urea and sarcosine:

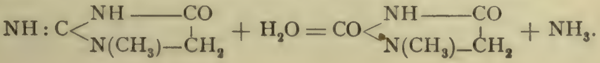


$$NH:C<\begin{matrix}NH_2\\ N(CH_3)-CH_2-CO_2H\end{matrix} + H_2O = CO<\begin{matrix}NH_2\\ NH_2\end{matrix} + \begin{matrix}NH(CH_3)\\ |\\ CH_2.CO_2H.\end{matrix}$$

Ammonia is liberated at the same time, and methyl hydantoïn is formed. (3) When its aqueous solution is heated with mercuric oxide, creatine becomes oxalic acid and methyl guanidine. (4) With acetic anhydride it yields *diacetyl creatine*, $NH.C<\begin{matrix}NH.CO.CH_3\\ N(CH_3).CH_2.CO.O.COCH_3\end{matrix}$, melting at 165° (A. **284**, 51).

Creatinine, methyl glycocyamidine, $NH=C<\begin{matrix}NH\text{——}CO\\ N(CH_3)CH_2\end{matrix}$, occurs constantly in urine (about 0.25 per cent.), and is readily obtained from creatine by evaporating its aqueous solution, especially when acids are present. It crystallizes in rhombic prisms, and is much more soluble than creatine, in water and alcohol. It is a strong base, which can expel ammonia from ammonium salts and yields well crystallized salts with acids. Its compound with zinc chloride, $(C_4H_7N_3O)_2.ZnCl_2$, is particularly characteristic. Zinc chloride precipitates it from creatinine solutions as a crystalline powder, dissolving with difficulty in water.

(1) Bases cause creatinine to absorb water and become creatine again. (2) Boiled with baryta water it decomposes into methyl hydantoïn and ammonia:

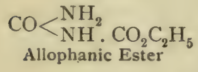


$$NH:C<\begin{matrix}NH\text{——}CO\\ N(CH_3)-CH_2\end{matrix} + H_2O = CO<\begin{matrix}NH\text{——}CO\\ N(CH_3)-CH_2\end{matrix} + NH_3.$$

(3) When boiled with mercuric oxide it breaks up like creatine into methyl-guanidine and oxalic acid.

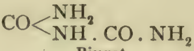
When creatinine is heated with alcoholic ethyl iodide, the ammonium iodide of ethyl creatinine, $C_4H_7(C_2H_5)N_3O.I$, is produced. Silver oxide converts this into the ammonium base, $C_4H_7(C_2H_5)N_3O.OH$.

Guaneïdes of Carbonic Acid.—Guanoline, guanyl urea, biguanide, and probably dicyandiamide, corresponding to allophanic ester (p. 403), biuret (p. 403), and cyanurea (p. 403), are derivatives of the guaneïde of carbonic acid. This is not known, and probably cannot exist:



$\mathrm{CO}<\begin{matrix}\mathrm{NH_2}\\ \mathrm{NH.CO_2C_2H_5}\end{matrix}$

Allophanic Ester

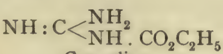


$\mathrm{CO}<\begin{matrix}\mathrm{NH_2}\\ \mathrm{NH.CO.NH_2}\end{matrix}$

Biuret

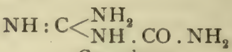
$\mathrm{CO}<\begin{matrix}\mathrm{NH_2}\\ \mathrm{NHCN}\end{matrix}$

Cyanurea



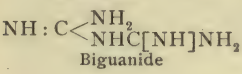
$\mathrm{NH:C}<\begin{matrix}\mathrm{NH_2}\\ \mathrm{NH.CO_2C_2H_5}\end{matrix}$

Guanoline



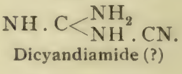
$\mathrm{NH:C}<\begin{matrix}\mathrm{NH_2}\\ \mathrm{NH.CO.NH_2}\end{matrix}$

Guanylurea



$\mathrm{NH:C}<\begin{matrix}\mathrm{NH_2}\\ \mathrm{NHC[NH]NH_2}\end{matrix}$

Biguanide



$\mathrm{NH.C}<\begin{matrix}\mathrm{NH_2}\\ \mathrm{NH.CN.}\end{matrix}$

Dicyandiamide (?)

Guanoline, Guanidocarbonic Ester, $\mathrm{NH:C}<\begin{matrix}\mathrm{NH_2}\\ \mathrm{NHCO_2C_2H_5}\end{matrix} + \frac{1}{2}H_2O$, melts, when dehydrated, at 114°. It is obtained from the reaction-product arising from chlorcarbonic ester and guanidine, *guanido-dicarbonic diethyl ester*, $\mathrm{NH:C}<\begin{matrix}\mathrm{NH.CO_2C_2H_5}\\ \mathrm{NH.CO_2C_2H_5}\end{matrix}$, through the action of ammonia (B. **7**, 1588).

Dicyandiamidine, $\mathrm{NH:C}<\begin{matrix}\mathrm{NH_2}\\ \mathrm{NH.CO.NH_2}\end{matrix}$, *Guanyl Urea*, is formed (1) by the action of dilute acids upon dicyandiamide or cyanamide, or (2) by fusing a guanidine salt with urea (B. **7**, 446). It is a strongly basic, crystalline substance. It forms a copper derivative having a characteristic red color. When digested with baryta water it decomposes into CO_2, $2NH_3$, and urea (B. **20**, 68).

Biguanide, *Guanyl Guanidine*, $\mathrm{NH:C}<\begin{matrix}\mathrm{NH_2}\\ \mathrm{NHC(NH)NH_2}\end{matrix}$, is formed (1) on heating guanidine hydrochloride to 180–185°; (2) when cyanguanidine is heated with ammonium chloride. It is a strongly alkaline base, forming a copper derivative with characteristic red color. Chloroform and caustic alkali convert it into *formoguanamine* (p. 412).

Dicyandiamide, *Param*, *Cyanguanidine*, $\mathrm{NH:C}<\begin{matrix}\mathrm{NH_2}\\ \mathrm{NH.CN}\end{matrix}$, melting at 205°, results from the polymerization of cyanamide upon long standing or by evaporation of its aqueous solution. Ammonia converts it into biguanide, and dilute acids to guanylurea. Formerly, the formula $\mathrm{NH_2.C}\begin{matrix}\diagup\mathrm{N}\diagdown\\ \diagdown\mathrm{N}\diagup\end{matrix}\mathrm{C.NH_2}$, or $\mathrm{NH:C}<\begin{matrix}\mathrm{NH}\\ \mathrm{NH}\end{matrix}>\mathrm{C:NH}$, was ascribed to this compound. Its behavior with piperidine, with which it combines to form a *biguanide* derivative, indicates the cyanamidine formula (B. **24**, 899; **25**, 525). See guanazole, p. 415.

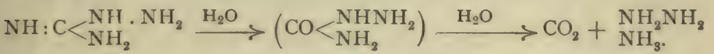
NITRO-GUANIDINE AND ITS TRANSPOSITION PRODUCTS.

Nitroguanidine is the starting-out material for the preparation of a series of remarkable guanidine and urea derivatives (Thiele, A. **270**, 1; **273**, 133; B. **26**, 2598, 2645).

Nitroguanidine, $\mathrm{NH:C}<\begin{matrix}\mathrm{NHNO_2}\\ \mathrm{NH_2}\end{matrix}$, melting at 240°, results on treating guanidine with a mixture of nitric and sulphuric acids. It dissolves with difficulty in cold water, more readily in hot water, and very copiously in alkalies, because of its feeble acid character.

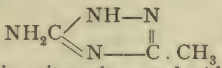
Nitroso-guanidine, $NH : C{<}\begin{smallmatrix}NH \,.\, NO\\ NH_2\end{smallmatrix}$(?), is produced by reducing nitroguanidine with zinc dust and sulphuric acid. It consists of yellow needles, exploding at 160–165°.

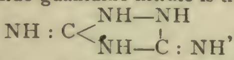
Amido-guanidine, $NH : C{<}\begin{smallmatrix}NHNH_2\\ NH_2\end{smallmatrix}$, results when nitro- and nitroso-guanidine are reduced with zinc dust and acetic acid. Amido-guanidine decomposes readily when in a pure condition, and when boiled with acids it breaks down, with the temporary production of semicarbazide (p. 405), into carbonic acid, ammonia, and *hydrazine*, which can therefore be conveniently prepared in this manner:

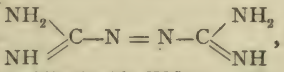


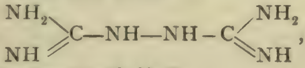
$$NH:C{<}\begin{smallmatrix}NH \,.\, NH_2\\ NH_2\end{smallmatrix} \xrightarrow{H_2O} \left(CO{<}\begin{smallmatrix}NHNH_2\\ NH_2\end{smallmatrix}\right) \xrightarrow{H_2O} CO_2 + \begin{smallmatrix}NH_2NH_2\\ NH_3.\end{smallmatrix}$$

Amido-guanidine forms well-crystallized compounds with dextrose, galactose, and lactic acid (B. **28**, 2613).

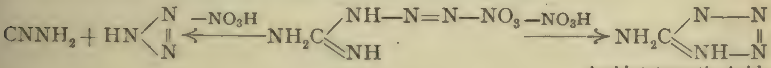
Amidomethyl-triazole,  $NH_2C{<}\begin{smallmatrix}NH—N\\ \|\\ N——C \,.\, CH_3\end{smallmatrix}$ (?), melting at 148°, is produced when acetylamido-guanidine nitrate is treated with soda.

Guanazole,  $NH : C{<}\begin{smallmatrix}NH—NH\\ |\\ NH—C : NH\end{smallmatrix}$, melting at 206°, results when dicyandiamide (see above) is heated with hydrazine hydrochloride in alcoholic solution to 100° (B. **27**, R. 583).

Azodicarbondiamidine,  $\begin{smallmatrix}NH_2\\ NH\end{smallmatrix}{>}C—N = N—C{<}\begin{smallmatrix}NH_2\\ NH\end{smallmatrix}$, is obtained as nitrate when amido-guanidine nitrate is oxidized with $KMnO_4$. The azonitrate forms a yellow, sparingly soluble, crystalline powder, exploding at 180–184°. It passes into azodicarbonamide (p. 405) when boiled with water.

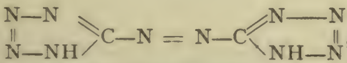
Hydrazodicarbonamidine,  $\begin{smallmatrix}NH_2\\ NH\end{smallmatrix}{>}C—NH—NH-C{<}\begin{smallmatrix}NH_2\\ NH\end{smallmatrix}$, results as nitrate when azodicarbonamidine nitrate is reduced with H_2S.

Diazoguanidine Dinitrate, $NH : C{<}\begin{smallmatrix}NHN = N—NO_3\\ NH_2\end{smallmatrix}$, melting at 129°, consists of colorless crystals, readily soluble in water and alcohol, but insoluble in ether. It is obtained when potassium nitrite acts on the nitric acid solution of amidoguanidine nitrate. Caustic soda converts it into *cyanamide* and *hydronitric acid*, and by acids in addition in part into *amidotetrazotic acid*, melting at 203°. This acid, with its decomposition products, will be mentioned after tetrazole:



$$CNNH_2 + HN{<}\begin{smallmatrix}N\\ \|\\ N\end{smallmatrix} \xleftarrow{-NO_3H} NH_2C{<}\begin{smallmatrix}NH—N{=}N—NO_3\\ NH\end{smallmatrix} \xrightarrow{-NO_3H} NH_2C{<}\begin{smallmatrix}N——N\\ \|\\ NH—N\end{smallmatrix}$$

Amidotetrazotic Acid.

Azotetrazole,  $\begin{smallmatrix}N—N\\ \|\\ N—NH\end{smallmatrix}{>}C—N = N—C{<}\begin{smallmatrix}N——N\\ \|\\ NH—N\end{smallmatrix}$, results when amidotetrazotic acid is oxidized by potassium permanganate.

Isocyantetrabromide or *Tetrabromformalazine*, $Br_2C = N — N = CBr_2$, melting at 42°, is produced when hydrazotetrazole, the reaction-product of azotetrazole, is treated with bromine (B. **26**, 2645). With alkalies isocyantetrabromide apparently yields *isocyanoxide*, $CO = N — N = CO$ (?), or a polymeride of it. Should an oxidizable body like alcohol be present, isocyanogen, $C = N — N = C$(?), is produced. This substance has an odor very much like that of isonitrile.

NITRILES AND IMIDES OF CARBONIC AND THIOCARBONIC ACIDS.

The nitriles, *cyanic acid*, *thiocyanic acid*, *cyanogen chloride*, and *cyanamide*, stand in a systematic and genetic connection with carbamic acid, thiocarbamic acid, urea chloride, and urea, as well as with thiourea:

$NH_2.COOH$	NH_2COSH	NH_2COCl	NH_2CONH_2	NH_2CSNH_2
Carbamic Acid	Thiocarbamic Acid	Urea Chloride	Urea	Thio-urea

$N\equiv C.OH$	$N\equiv C.SH$	$N\equiv CCl$	$N\equiv C.NH_2$
Cyanic Acid	Thiocyanic Acid	Cyanogen Chloride	Cyanamide.

The empiric formulas of cyanic acid, $CNOH$, thio-cyanic acid, $CNSH$, and cyanamide, CN_2H_2, have each another structural formula:

$HN=C=O$	$HN=CS$	$NH=C=NH$
Isocyanic Acid, Carbimide	Isothiocyanic Acid Thiocarbimide	Carbodi-imide.

Indeed, alkylic derivatives are known which correspond to both formulas of each of these bodies. The isothiocyanic esters, or *mustard oils*, may be especially mentioned. The constitution of free cyanic acid, and of cyanamide, has not yet been determined with certainty. The normal formula, $N\equiv C.SH$, is universally attributed to thiocyanic or sulphocyanic acid.

The remarkable tendency of cyanic acid and cyanamide to polymerization is particularly noteworthy. Experience with other classes of compounds would indicate that this is an argument for unsymmetrical constitution—*i. e.*, for the normal cyanogen formulas of the polymerizing compounds. The more unsymmetrically unsaturated bodies are constructed, the greater is their tendency to polymerize to symmetrical and generally ring-shaped atomic complexes.

When the simple derivatives of cyanic acid have been discussed, then the corresponding trimolecular polymerides will be described.

Numerous compounds containing the cyanogen group have been described and discussed in the preceding pages as nitriles of carboxylic acids (p. 283), oxy- and ketonic acids (pp. 349, 370). The simplest body, *hydrogen cyanide* or *prussic acid* (p. 228), has been discussed with formic acid. Cyanic acid sustains a relation to prussic acid similar to that of carbonic acid to formic acid.

OXYGEN DERIVATIVES OF CYANOGEN, THEIR ISOMERIDES AND POLYMERIDES.

Cyanic Acid, $N\equiv C.OH$, isomeric with fulminic acid or carbyloxime (p. 237), is obtained by heating polymeric cyanuric acid. The vapors which distil over are condensed in a strongly cooled receiver.

The acid is only stable below 0°, and is a mobile, very volatile liquid, which reacts strongly acid, and smells very much like glacial acetic acid. It produces blisters upon the skin. At about 0°, the aqueous solution is rapidly converted into carbon dioxide and ammonia:

$$CONH + H_2O = CO_2 + NH_3.$$

At 0°, the aqueous cyanic acid passes rapidly into the polymeric *cyamelide*—a white, porcelain-like mass, which is insoluble in water, and when distilled reverts to cyanic acid. Above 0°, the conversion of liquid cyanic acid into cyamelide occurs, accompanied by explosive foaming. Cyanic acid dissolves in alcohols, yielding esters of allophanic acid.

Potassium Cyanate, Potassium Isocyanate, *ordinary cyanate of potassium*, $N : C . OK$, or $O : C : NK$, is formed in the oxidation of potassium cyanide in the air, or with some oxidant like lead oxide, minium, potassium permanganate, or sodium hypochlorite (B. **26**, R. 779). It is most conveniently made by heating small portions (3–5 gm.) of an intimate mixture of 100 parts potassium ferrocyanide and 75 parts of potassium bichromate in an iron dish, when NH_3 should not be set free (B. **26**, 2438). It results, too, on conducting dicyanogen or cyanogen chloride into caustic potash (B. **23**, 2201). The salt crystallizes in shining leaflets, resembling potassium chlorate, or in quadratic plates (B. **27**, 837), and dissolves readily in cold water, but with more difficulty in hot alcohol. In aqueous solution it decomposes rapidly into ammonia and potassium carbonate.

Potassium isocyanate precipitates aqueous solutions of the heavy metals. The lead, silver, and mercurous salts are white, the cupric salt is green in color.

The transpositions of the potassium salt with ethyl sulphate, and the silver salt with ethyl iodide, forming isocyanic esters, would indicate their formulas to be: $O : C : NK$ and $O : C : N . Ag$.

Ammonium cyanate, $CN . O . NH_4$ or $CO : N(NH_4)$, is a white crystalline powder, formed by contact of cyanic acid vapors with dry ammonia. Caustic potash decomposes it into potassium isocyanate and ammonia. On evaporating the aqueous solution it passes into isomeric urea (p. 396).

The cyanates of the primary and secondary amines are similarly converted into alkylic ureas, whereas the salts of the tertiary amines remain unchanged.

Esters of Normal Cyanic Acid (*Cyanetholines*) are not known (A. **287**, 310). Imidocarbonic acid ethers (p. 404) are produced when cyanogen chloride acts upon sodium alcoholates in alcoholic solution.

Esters of Isocyanic Acid, Alkyl Carbimides or *Alkyl Cyanates.*—Würtz prepared these, in 1848, (1) by distilling potassium ethyl sulphate with potassium isocyanate:

$$SO_4K(C_2H_5) + CO : NK = CO : N . C_2H_5 + SO_4K_2.$$

Esters of isocyanuric acid are formed at the same time, in consequence of polymerization. (2) Isocyanic esters are produced, too, by oxidizing the carbylamines with mercuric oxide:

$$C_2H_5 . NC + O = C_2H_5 . N : CO;$$

and (3) by the action of silver isocyanate upon alkyl iodides at low temperatures:

$$C_2H_5I + CO : NAg = CO : N . C_2H_5 + AgI.$$

These esters are volatile liquids, boiling without decomposition, and possessing a very disagreeable, penetrating odor, which provokes tears. They dissolve without decomposition in ether. On standing they pass rather rapidly into the polymeric isocyanuric esters.

Methyl Isocyanic Ester, $CO : N . CH_3$, methyl isocyanate, methyl carbimide, boils at 44°.

Ethyl Isocyanic Ester, $CO : N . C_2H_5$, boils at 60°.

Allyl Isocyanic Ester, $CO : N . C_3H_5$, boils at 82°.

Transpositions.—In all their reactions they behave like carbimide derivatives. (1) Heated with KOH they become primary amines and potassium carbonate (p. 162). This is the method Würtz used when he first discovered them.

(2) Acids in aqueous solution behave similarly:

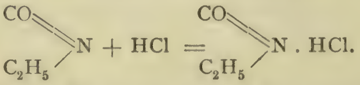
$$CO : N . C_2H_5 + H_2O + HCl = CO_2 + C_2H_5 . NH_2 . HCl.$$

(3) With the amines and ammonia they yield alkylic ureas (see these). (4) Water breaks them up at once into CO_2 and dialkylic ureas. In this decomposition amines form first, CO_2 being set free, and these combine with the excess of isocyanic ester to dialkylic ureas (see these).

(5) Fatty acids convert them into alkylic, primary acid amides (p. 264). CO_2 is simultaneously evolved. (6) Acid anhydrides convert them into alkylic secondary acid amides (p. 264).

(7) The esters of isocyanic acid unite with alcohol, yielding esters of carbamic acid (p. 394).

(8) As derivatives of ammonia the isocyanic esters are capable of combining directly with the haloid acids. The products are *urea chlorides* (p. 395), from which the isocyanic esters are again separated by distillation with lime:

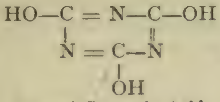
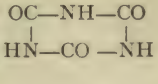


$$\left.\begin{matrix}CO\\C_2H_5\end{matrix}\right> N + HCl = \left.\begin{matrix}CO\\C_2H_5\end{matrix}\right> N . HCl.$$

Acetyl Isocyanate, $CONCOCH_3$, boiling at about 80°, results from the action of acetyl chloride upon fulminating mercury (p. 238). That it very probably is acetyl isocyanate would seem to be indicated by its transpositions with alcohol and ammonia to acetyl urethane (p. 395), and mono-acetyl urea (p. 400) (B. 23, 3510).

CYANURIC ACID AND ITS ALKYLIC DERIVATIVES.

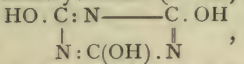
Just as with cyanic acid, so here with tricyanic acid, two structural cases are possible:

(1)  and (2) 

Normal Cyanuric Acid

Isocyanuric Acid or Tricarbimide.

Ordinary cyanuric acid is most probably constituted according to formula (1), because when sodium alcoholates act upon cyanuric bromide, $C_3N_3Br_3$, and alkyl iodides upon ordinary silver cyanate, esters of normal cyanuric acid result (below). Isocyanuric acid (formula 2) is not known in a free state. Upon saponifying the isocyanuric esters (p. 420), constituted according to the carbimide formula (2), ordinary cyanuric acid invariably results (B. **20**, 1056).

Cyanuric Acid, , was observed by Scheele in the dry distillation of uric acid. It is produced (1) by heating tricyanogen chloride $C_3N_3Cl_3$ or tricyanogen bromide (B. **16**, 2893) with water to 120–130°, or with alkalies. (2) Dilute acetic acid added to a solution of potassium isocyanate gradually separates primary potassium isocyanate, $C_3N_3O_3H_2K$, from which mineral acids release cyanuric acid. (3) It appears, too (*a*) on heating urea (*b*) or carbonyl diurea (p. 404); (*c*) on conducting chlorine over urea heated to 130–140°; (*d*) when urea is heated with a solution of phosgene in toluene to 190–230° (B. **29**, R. 866).

$$(a)\ 3CO(NH_2)_2 = C_3O_3N_3H_3 + 3NH_3$$
$$(b)\ NH_2CONH.CO.NHCONH_2 = C_3O_3N_3H_3 + NH_3$$
$$(c)\ 3Cl + 3CO(NH_2)_2 = C_3O_3N_3H_3 + 2NH_4Cl + HCl + N$$
$$(d)\ 3COCl_2 + 3CO(NH_2)_2 = 2C_3O_3N_3H_3 + 6HCl.$$

Cyanuric acid crystallizes from aqueous solution with 2 molecules of water ($C_3N_3O_3H_3 + 2H_2O$) in large rhombic prisms. It is soluble in 40 parts of cold water, and easily soluble in hot water and alcohol. When boiled with acids it decomposes into carbonic acid and ammonia. When distilled it breaks up into cyanic acid. PCl_5 converts it into tricyanogen chloride.

Cyanuric acid is tribasic. A characteristic salt is the trisodium salt, $C_3N_3O_3Na_3$.

Normal Cyanuric Esters are formed (1) by the action of cyanogen chloride upon sodium alcoholates.

(2) A simpler procedure is to act upon the sodium alcoholates with cyanuric chloride or bromide (B. **18**, 3263 and **19**, 2063).

(3) The normal cyanuric esters are also formed by the action of alkyl iodides upon silver cyanurate, $C_3N_3(OAg)_3$, at 100°.

Methyl Cyanuric Ester melts at 135° and boils at 263°.

Ethyl Cyanuric Ester melts at 29° and boils unaltered at 275°.

The normal cyanuric esters, on digesting with the alkalies, break up into cyanuric acid and alcohol. They combine with six atoms of bromine. PCl_5 converts them into cyanuric chloride. Boiling gradually changes them to isocyanuric esters.

Partial saponification of the normal cyanuric esters by NaOH or $Ba(OH)_2$ gives rise to normal dialkyl cyanuric acids; these, when heated, rearrange themselves into dialkyl isocyanuric acids (B. 19, 2067):

Dimethyl Cyanuric Acid, $C_3N_3(O.CH_3)_2.OH$, melts at 160–180°, and suddenly passes into *dimethyl isocyanuric acid* (melting at 222°).

Cyanuric Triacetate, $C_3N_3(O.C_2H_3O)_3$, melts with partial decomposition at 170°, and is prepared from silver cyanurate and acetyl chloride.

Esters of Isocyanuric Acid, $C_3O_3(N.CH_3)_3$, *Tricarbimide esters*, are formed together with the isocyanic esters, when the latter are prepared by the distillation of KCNO with potassium ethyl or methyl sulphate. We have already spoken of their formation as a result of the molecular transposition of the cyanuric esters. Hence they are formed together with these, or appear in their stead in energetic reactions—*e g.*, in the distillation of potassium cyanate with ethyl sulphates, or when silver cyanurate is acted upon by alkyl iodides (see above). They are solid crystalline bodies, soluble in water, alcohol, and ether, and may be distilled without decomposition. They pass into primary amines and potassium carbonate when boiled with alkalies, similar to the isocyanates:

$$C_3O_3(N.CH_3)_3 + 6KOH = 3CO_3K_2 + 3NH_2.CH_3.$$

Methyl Isocyanuric Ester, Methyl Tricarbimide, $C_3O_3(N.CH_3)_3$, melts at 175° and boils undecomposed at 296°.

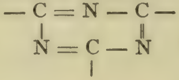
Ethyl Isocyanuric Ester, $C_3O_3(N.C_2H_5)_3$, melts at 95° and boils at 276°. It volatilizes with steam.

Dialkyl Isocyanuric Esters, or Isocyanuric Dialkyl Esters, see dimethyl cyanuric acid.

HALOGEN COMPOUNDS OF CYANOGEN AND THEIR POLYMERIDES.

The cyanogen haloids may be viewed either as the chloride, bromide and iodide of cyanic acid, or as the nitriles of chlor-, brom-, or iodo-carbonic acids which cannot exist:

(Cl.COOH)	Cl.CONH$_2$	ClC ≡ N
Chlorcarbonic Acid	Urea Chloride	Cyanogen Chloride.

They result by the action of the halogens upon metallic cyanides (mercuric cyanide), or upon aqueous prussic acid. The chloride and bromide can condense to tricyanides, in which we assume the presence of the tricyanogen group, $C_3N_3 =$  $\begin{array}{c} -C=N-C- \\ | \qquad\quad \| \\ N=C-N \\ | \end{array}$, the radical of cyanuric acid.

Cyanogen Chloride, CNCl, is produced by acting with chlorine upon aqueous hydrocyanic acid or upon a cold mercuric cyanide solution. It is a mobile liquid, solidifying at −5°, and boiling at +15°. It passes into cyanuric chloride on preservation. With ammonia, it yields ammonium chloride and cyanamide, $CN.NH_2$. Alkalies decompose it into metallic cyanides and isocyanates.

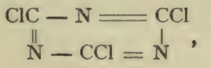
Cyanogen Bromide, CNBr, melting at 52° and boiling at 61°, is produced on adding a potassium cyanide solution drop by drop to bromine, well-cooled (B. **29**, 1822).

Cyanogen Iodide, CNI, sublimes at 45°, without melting, in brilliant white needles.

These compounds are sparingly soluble in water, but they dissolve readily in alcohol and ether. Their vapors have a penetrating odor, provoking tears, and acting as powerful poisons.

Cyanuric haloids are converted into cyanuric acid when heated with water.

Tricyanogen Chloride, *Cyanuric Chloride*, *Solid Chlorcyanogen*,



$$\begin{array}{c} ClC - N = CCl \\ \| \qquad\quad | \\ N - CCl = N \end{array},$$

is produced when liquid cyanogen chloride is kept in sealed tubes. In the polymerization of cyanogen chloride $+189.05$ C. are liberated (C. 1897, **1**, 284). It is formed directly by leading chlorine into an ethereal solution of CNH, or into anhydrous hydrocyanic acid exposed to direct sunlight (B. **19**, 2056). It appears, too, in the distillation of cyanuric acid, $C_3O_3N_3H_3$, with phosphorus pentachloride (A. **116**, 357). It melts at 146° and boils at 190°. It is not very soluble in cold water, but readily in alcohol and ether. When boiled with water or alkalies, it breaks up into hydrochloric and cyanuric acids (B. **19**, R. 599).

Cyanuric Bromide, $C_3N_3Br_3$, is produced (1) from bromcyanogen in the presence of a little bromine. (2) On heating the anhydrous bromide or its ethereal solution in sealed tubes to 130–140°. (3) By heating dry yellow or red prussiate of potash with bromine at 250° (B. **16**, 2893) or (4) on conducting HBr into the ethereal solution of CNBr (B. **18**, 3262). It melts above 300°, and is volatile at higher temperatures.

Cyanuric Iodide, $C_3N_3I_3$, is produced by the action of hydriodic acid upon cyanuric chloride. It is a dark brown, insoluble powder. At 200° it readily breaks up into iodine and paracyanogen, $(CN)_n$ (B. **19**, R. 599).

SULPHUR COMPOUNDS OF CYANOGEN, THEIR ISOMERIDES AND POLYMERIDES.

The thiocyanic acids are:

$N \equiv C{-}SH$	and	$S = C = NH$
Thiocyanic Acid, Sulphocyanic Acid		**Isothiocyanic Acid, Sulphocarbimide.**

These correspond to the two isomeric cyanic acids (p. 416).

The known thiocyanic acid and its salts (having the group NC.S—) are constituted according to the first formula. Its salts are obtained from the cyanides by the addition of sulphur, just as the isocyanates result by the absorption of oxygen. The different union of sulphur and oxygen in this instance is noteworthy:

$$CNK + O = CO:NK \qquad CNK + S = CN.SK.$$

Isothiocarbimide, CS:NH, and its salts are not known. Its esters (the mustard oils) do, however, exist and are isomeric with those of sulphocyanic acid.

Thiocyanic Acid, Sulphocyanic Acid, CN . SH, occurs in small quantities in the human stomach (B. **28,** 1318), and is obtained by distilling its potassium salt with dilute sulphuric acid, or decomposing the mercury salt with dry H_2S or HCl. It is a liquid with a penetrating odor. When removed from a cooling mixture, it polymerizes to a yellow amorphous body, giving out much heat at the same time (B. **20,** R. 317). It is soluble in water and alcohol. Its solutions react acid. The free acid, and also its salts, color solutions of ferric salts a dark red. This is an exceedingly delicate reaction, which, when CNSK is used, is based on the formation of $(CNS)_6Fe_2 + 9CNSK$ (B. **22,** 2061). It is this reaction which has given the name rhodanides (from *ῥόδον*, rose), to sulphocyanides. The free acid decomposes readily, especially in the presence of strong acids, into hydrogen cyanide and persulphocyanic acid, $C_2N_2S_3H_2$.

The *alkali thiocyanates*, like the isocyanates, are obtained by fusing the cyanides with sulphur.

Potassium Thiocyanate, CN . SK, sulphocyanate of potash, crystallizes from alcohol in long, colorless prisms, which deliquesce in the air. The *sodium salt* is very deliquescent, and occurs in the saliva and urine of different animals.

Ammonium Thiocyanate, $CN . S . NH_4$, is formed on heating prussic acid with yellow ammonium sulphide, or a solution of ammonium cyanide with sulphur. It is most readily obtained by heating CS_2 with alcoholic ammonia:

$$CS_2 + 4NH_3 = CN . S . NH_4 + (NH_4)_2S.$$

The salt crystallizes in prisms, which readily dissolve in water and alcohol. It melts at 150°, and at 170-180° molecular transposition into thiourea occurs (similar to ammonium cyanate, p. 397).

The salts of the heavy metals are mostly insoluble. The *mercury salt*, $(CN . S)_2$-Hg, is a gray, amorphous precipitate, which burns on ignition and swells up strongly (Pharaoh's serpents). The *silver salt*, CNSAg, is a precipitate similar to silver chloride. The volumetric method of Volhard is based on its production (A. **190,** 1). *Lead sulphocyanide*, $(CNS)_2Pb$.

Cyanogen Sulphide, $(CN)_2S$, is formed when cyanogen iodide in ethereal solution acts on silver thiocyanate.

Cyanogen sulphide forms rhombic plates, melting at 65° and subliming at 30°. It dissolves in water, alcohol and ether.

Addition: Persulphocyanic Acid, Xanthane Hydride, $C_2N_2H_2S_3$, consists of yellow prisms, sparingly soluble in water. It is a decomposition product of hydrogen sulphocyanide (J. pr. Ch. [2] **38,** 368). Alkalies change it to *dithiocyanic acid*, $C_2N_2H_2S_2$ (A. **179,** 204).

Pseudo-Cyanogen Sulphide, $C_3N_3HS_3$(?), is formed in the oxidation of potassium sulphocyanide with nitric acid or chlorine. It is a yellow, amorphous powder, insoluble in water, alcohol and ether. It dissolves with a yellow color in alkalies.

Kanarine is similar to and probably identical with pseudo-cyanogen sulphide. It is obtained from KCNS by electrolysis, or by oxidation with $KClO_3$ and HCl (B. **17,** R. 279, 522, and **18,** R. 676). It is applied as a yellow or orange dye for wool and does not require a mordant.

Esters of *normal sulphocyanic acid* are obtained (1) by distilling organic salts of sulphuric acid in concentrated aqueous solution with potassium sulphocyanide, or by heating with alkyl iodides:

$$CN . SK + C_2H_5I = CN . S . C_2H_5 + KI.$$

Further, (2) by the action of CNCl upon salts of the mercaptans:

$$C_2H_5 . SK + CNCl = C_2H_5 . S . CN + KCl.$$

They are liquids, not soluble in water, and possess a leek-like odor. Nascent hydrogen (zinc and sulphuric acid) converts them into hydrocyanic acid and mercaptans:

$$CN . S . C_2H_5 + H_2 = CNH + C_2H_5 . SH.$$

On digesting with alcoholic potash the reaction is:

$$CN . S . C_2H_5 + KOH = CN . SK + C_2H_5 . OH.$$

The isomeric mustard oils do not afford any potassium sulphocyanate. Boiling nitric acid oxidizes them to alkylsulphonic acids with separation of the cyanogen group. This would prove that the alkyl group in these bodies is linked directly to sulphur.

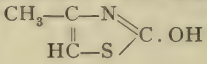
Methyl Thiocyanic Ester, $CN . S . CH_3$, has a specific gravity 1.088 at 0°. When heated to 180–185° it is converted into the isomeric methyl-isothiocyanic ester. This conversion is more readily effected with allyl sulphocyanide (see allyl mustard oil, p. 425).

Ethyl Thiocyanic Ester, $CN . S . C_2H_5$, boils at 142°.

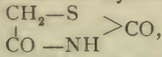
Isopropyl Thiocyanic Ester, $CN . S . C_3H_7$, boils at 152–153°.

Allyl Thiocyanic Ester, $CN . S . C_3H_5$, boils at 161° and rapidly changes to isomeric allyl mustard oil, $CS : N . C_3H_5$.

Ketone and Fatty Acid Sulphocyanides.—Mention may be made in this connection of sulphocyanacetone, and sulphocyanacetic acid.

Sulphocyan-acetone, $CN . S . CH_2 . CO . CH_3$, is formed from barium sulphocyanide and chloracetone (p. 216). It is an oil with scarcely any color. Its sp. gr. equals 1.180 (20°). It is somewhat soluble in water, and very readily soluble in ether. The alkali carbonates rearrange it into *methyl-oxythiazole*,  (B. **25**, 3648).

Thiocyanacetic Acid, $CNS . CH_2 . CO_2H$, **Sulphocyanacetic Acid**, is formed by the action of chloracetic acid upon KCNS. It is a thick oil. Its *ethyl ester*, from chloracetic ester, boils at about 220° C.

On boiling the latter with concentrated hydrochloric acid, it takes up water, loses alcohol, and rhodanacetic acid, , is formed (A. **249**, 27).

These heterocyclic bodies, derived from the products of the interaction of ammonium sulphocyanide with α-chlorketones and α-chlor-fatty acids, belong to the class of *thiazoles*.

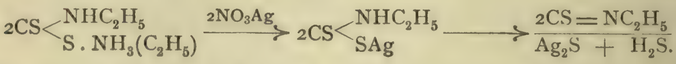
Mustard Oils, *Esters of Isothiocyanic Acid, Alkyl Thiocarbimides.*

The esters of isothiocyanic acid, $CS : NH$, not known in a free condition, are termed mustard oils, from their most important representative. They may also be considered as sulphocarbimide derivatives.

They are produced (1) by the rearrangement of the isomeric *alkyl sulphocyanides* on the application of heat (p. 422):

$$CNS . C_3H_5 \longrightarrow CS = NC_3H_5.$$

(2) By mixing carbon disulphide with primary amines in alcoholic or, better, ethereal solution. By evaporation we get amine salts of alkyl carbamic acids (B. **23**, 282). On adding silver nitrate, mercuric chloride (B. **29**, R. 651) or ferric chloride (B. **8**, 108) to the aqueous solution of these salts, formed with primary amines, and then heating to boiling, the metallic compounds first precipitated decompose into metallic sulphides, hydrogen sulphide and mustard oils, which distil over with steam.



$$2CS<^{NHC_2H_5}_{S.NH_3(C_2H_5)} \xrightarrow{2NO_3Ag} 2CS<^{NHC_2H_5}_{SAg} \longrightarrow \frac{2CS=NC_2H_5}{Ag_2S + H_2S.}$$

Hofmann's mustard oil test for the detection of primary amines (p. 166) is based on this behavior (B. **1**, 170).

Iodine, too, forms mustard oils from the amine salts of the dithiocarbamic acids, but the yield is small.

(3) By distilling the dialkylic thio-ureas (see these) with phosphorus pentoxide (B. **15**, 985), and (4) by heating the isocyanic esters with P_2S_5 (B. **18**, R. 72).

Properties.—The mustard oils are liquids, almost insoluble in water, and possess a very penetrating odor, which provokes tears. They boil at lower temperatures than the isomeric thiocyanic esters.

Transformations.—(1) When heated with hydrochloric acid to 100°, or with H_2O to 200°, they break up into *amines*, hydrogen sulphide, and carbon dioxide:

$$CS:N.C_2H_5 + 2H_2O = CO_2 + SH_2 + NH_2.C_2H_5.$$

(2) On heating with a little dilute sulphuric acid, *carbon oxysulphide*, COS, is formed, together with the amine. (3) When heated with carboxylic acids they yield monoacidyl acid amides and COS; and (4) with carbonic anhydrides, diacidyl amides and COS (B. **26**, 2648). (5) Nascent hydrogen (zinc and hydrochloric acid) converts them into thio-formaldehyde and primary amines:

$$CS:N.C_2H_5 + 2H_2 = CSH_2 + NH_2.C_2H_5.$$

(6) When the mustard oils are heated with absolute alcohol to 100°, or with alcoholic potash, they pass into sulph-urethanes. (7) They unite with ammonia and amines, yielding alkylic thio-ureas (see these). (8) Upon boiling their alcoholic solution with HgO or $HgCl_2$, a substitution of oxygen for sulphur occurs, with formation of esters of isocyanic acid. These immediately yield the dialkylic ureas with water (see p. 398). (9) Consult A. **285**, 154, for the action of the halogens upon the mustard oils.

Methyl Mustard Oil, $CS:N.CH_3$, methyl isosulphocyanic ester, methyl sulphocarbimide, melts at 34° and boils at 119°.

Ethyl Mustard Oil boils at 133°, and has a specific gravity 1.019 at 0°. **Propyl Mustard Oil** boils at 153°. **Isopropyl Mustard Oil** boils at 137°.

n-**Butyl Mustard Oil** boils at 167°. **Isobutyl Mustard Oil** boils at 162°.

Tertiary Butyl Mustard Oil boils at 142°. **n-Hexyl Mustard Oil** boils at 212°. **Heptyl Mustard Oil** boils at 238° (B. **29**, R. 651). Secondary **Octyl Mustard Oil** boils at 232°.

The most important of the mustard oils is the common or—

Allyl Mustard Oil, $CS:N.C_3H_5$, *Allyl Isosulphocyanic Ester.*—This is the principal constituent of ordinary mustard oil, which is obtained by distilling powdered black mustard seeds (from *Sinapis nigra*), or radish oil from *Cochlearia armoracia*, with water. Mustard seeds contain potassium *myronate* (see Glucosides), which in the presence of water, under the influence of a ferment, *myrosin* (also present in the seed), breaks up into grape sugar, primary potassium sulphate, and *mustard oil.*

The reaction occurs even at 0°, and there is a small amount of allyl sulphocyanate produced at the same time:

$$C_{10}H_{18}KNO_{10}S_2 = C_6H_{12}O_6 + SO_4KH + CS.N.C_3H_5.$$

Mustard oil is artificially prepared by distilling allyl iodide or bromide with alcoholic potassium or silver thiocyanate (Gerlich, A. **178**, 80):

$$CN.SK + C_3H_5I = CS.N.C_3H_5 + KI;$$

a molecular rearrangement occurs here (p. 52).

Pure allyl mustard oil is a liquid not readily dissolved by water, and boiling at 150.7°; its specific gravity equals 1.017 at 10°. It has a pungent odor and causes blisters upon the skin. When heated with water or hydrochloric acid the following reaction ensues:

$$CS:N.C_3H_5 + 2H_2O = CO_2 + SH_2 + NH_2.C_3H_5.$$

It unites with aqueous ammonia to form allyl thio-urea. When heated with water and lead oxide it yields diallyl urea.

Acidyl thiocarbimides are produced by the action of fatty-acid chlorides, dissolved in benzene, upon lead sulphocyanide. *Valeryl thiocarbimide*, $C_4H_9CO.N:CS$ (B. **29**, R. 85), and *Carboxethyl thiocarbimide*, $C_2H_5O.CO.N:CS$, boiling at 66° (21 mm.) (B. **29**, R. 514), were obtained in this manner.

Thio- or *sulphocyanuric Acid*, $C_3N_3(SH)_3$, corresponds to cyanuric acid. Isothiocyanuric acid is as little known as isocyanuric acid. Thiocyanuric acid results from cyanuric chloride (p. 421) and potassium sulphydrate. It consists of small yellow needles, which decompose but do not melt above 200°.

Its *esters* result when cyanuric chloride and sodium mercaptides interact, and by the polymerization of the thiocyanic esters, $CN.SR$, when heated to 180° with a little HCl. More HCl causes them to split up into cyanuric acid and mercaptans.

Methyl Ester, $C_3N_3(S.CH_3)_3$, melts at 188°, and with ammonia yields melamine (p. 427).

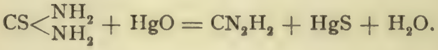
Isothiocyanuric Esters, $C_3S_3(NR')_3$, appear to have been formed by the polymerization of mustard oils with potassium acetate (B. **25**, 876).

CYANAMIDE AND THE AMIDES OF CYANURIC ACID.

Cyanamide, $CN . NH_2$, the nitrile of carbamic acid, absorbs water and passes into urea, the amide of carbamic acid. It manifests certain reactions, which would rather point to its being $NH = C = NH$, carbodiimide. A definite decision as to which of the two formula possibilities is the correct one cannot be given. It is formed (1) by the action of chlor- or brom-cyanogen upon an ethereal or aqueous solution of ammonia (Bineau, 1838; Cloëz and Cannizzaro, 1851):

$$CNCl + 2NH_3 = CN . NH_2 + NH_4Cl;$$

and also (2) by the desulphurizing of thiourea by means of mercuric chloride or lead peroxide (mercuric oxide is preferable) (B. **18,** 461):



$$CS{<}^{NH_2}_{NH_2} + HgO = CN_2H_2 + HgS + H_2O.$$

(3) By mixing urea with thionyl chloride:

$$CO(NH_2)_2 + SOCl_2 = CN_2H_2 + SO_2 + 2HCl.$$

It forms colorless crystals, easily soluble in water, alcohol, and ether, and melting at 40°. If heated it polymerizes to dicyandiamide and tricyan-triamide (melamine). It forms salts with strong acids, but these are decomposed by water. It also forms salts with metals. An ammoniacal silver nitrate solution throws down a yellow precipitate, CN_2Ag_2, from its solutions.

Transpositions.—(1) By the action of sulphuric acid or hydrochloric acid, it absorbs water and becomes urea. (2) H_2S converts it into thio-urea, and (3) NH_3 into guanidine (p. 411), while substituted guanidines are produced upon introducing the hydrochlorides of primary amines.

Alkylic Cyanamides are obtained (1) by letting cyanogen chloride act upon primary amines in ethereal solution; (2) by heating the corresponding thio-ureas with mercuric oxide and water.

Methyl Cyanamide, $CN_2H(CH_3)$ and **Ethyl Cyanamide,** $CN_2H(C_2H_5)$, are non-crystallizable, thick syrups with neutral reaction. They are readily converted into polymeric isomelamine derivatives.

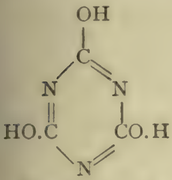
Allyl Cyanamide, $CN_2H(C_3H_5)$, called *Sinamine*, is obtained from allylthiourea. It is crystalline and polymerizes readily into triallylmelamine (see below).

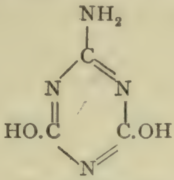
Dialkylic Cyanamides.—**Diethyl Cyanamide,** $CN . N(C_2H_5)_2$, is prepared by the interaction of silver cyanamide (which, therefore, has the formula $CN . NAg_2$) and ethyl iodide. It is a liquid, boiling at 186–190°. Boiling hydrochloric acid resolves it into CO_2, NH_3, and diethylamine, $NH(C_2H_5)_2$.

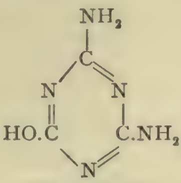
Another dialkylic carbodiimide is *Di-n-propyl-carbodi-imide*, $C(= N . C_3H_7)_2$, boiling at 177°, and obtained from sym. dipropylthiourea by means of HgO (B. **26,** R. 189).

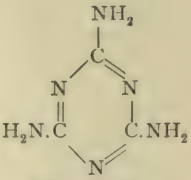
AMIDES OF CYANURIC ACID AND IMIDES OF ISOCYANURIC ACID.

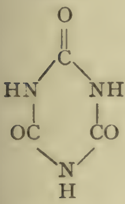
Three amides are derived from cyanuric acid, and three imides from hypothetical isocyanuric acid, the pseudo- form of cyanic acid:

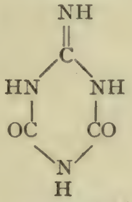

Normal Cyanuric Acid

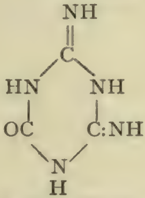

Cyanurmonamide, Ammelide

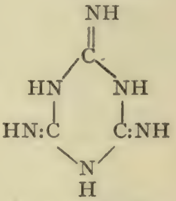

Cyanurdiamide, Ammeline


Cyanurtriamide, Melamine.


Isocyanuric Acid


Isocyanurmonamide, Melanuric Acid


Isocyanurdiimide, Isoammeline


Isocyanurtriimide, Isomelamine.

Melamine, $C_3N_3(NH_2)_3$ (see above), Cyanuramide, is obtained as sulphocyanide by: (1) The rapid heating of ammonium sulphocyanide (together with *melam* and *melem*). (2) The polymerization of cyanamide or dicyandiamide on heating to 150° (together with melam); (3) by heating methyl trithiocyanuric ester to 180° with concentrated ammonia; and (4) by heating cyanuric chloride to 100° with concentrated ammonia (B. 18, 2765):

$$C_3N_3Cl_3 + 6NH_3 = C_3N_3(NH_2)_3 + 3NH_4Cl.$$

Melamine is nearly insoluble in alcohol and ether. It crystallizes from hot water in shining monoclinic prisms. It sublimes on heating and decomposes into melam and NH_3. It forms crystalline salts with 1 equivalent of acid.

On boiling with alkalies or acids melamine splits off ammonia and passes successively into *ammeline*, $C_3H_5N_5O = C_3N_3(NH_2)_2.OH$ (a white powder insoluble in water, but soluble in alkalies and mineral acids) (B. 21, R. 789); *ammelide*, $C_3H_4N_4O_2 = C_3N_3(NH_2)(OH)_2$, a white powder that forms salts with both acids and bases, and finally cyanuric acid, $C_3N_3(OH)_3$ (B. 19, R. 341). Potassium cyanate is directly formed by fusing melamine with KOH.

Melanurenic Acid, $C_3H_4N_4O_2$, from melam and melem (p. 428), when heated with concentrated H_2SO_4, is probably identical with ammelide (B. 19, R. 341), or it is the isomeric isocyanurimide (B. 18, 3106).

Alkyl Derivatives of the Melamines.

While melamine is only known in one form as cyanurtriamide, two series of isomeric alkyl derivatives exist—obtained from normal melamine and hypothetical isomelamine:

(1) $C_3N_3(NHR')_3$ and $C_3H_3(NR'_2)_3$. Normal Alkylmelamines

(2) $C_3N_3H_3(NR')_3$. Isoalkylmelamines.

These are distinguished from each other not only in the manner of their preparation, but also in their transpositions.

(1) **Normal Alkylmelamines** are obtained from the trithiocyanuric esters, $C_3N_3(S.CH_3)_3$, and from cyanuric chloride, $C_3N_3Cl_3$, upon heating with primary and secondary amines (B. 18, R. 498): $C_3N_3Cl_3 + 3NH(CH_3)_2 = C_3N_3\left(N{<}^{CH_3}_{CH_3}\right)_3 + 3HCl$. Heating with concentrated hydrochloric acid causes them to split up into cyanuric acid and the constituent alkylamines.

Trimethylmelamine, $C_3N_3(NH.CH_3)_3$, dissolves readily in water, alcohol and ether. It melts at 130°. **Triethylmelamine**, $C_3N_3(NH.C_2H_5)_3$, crystallizes in needles and melts at 74° C.

Hexamethylmelamine, $C_3N_3[N(CH_3)_2]_3$, consists of needles, melting at 171° C. **Hexaethylmelamine**, $C_3H_3[N(C_2H_5)_2]_3$, is a liquid, and is decomposed by hydrochloric acid into cyanuric acid and 3 molecules of diethylamine.

(2) **Alkylisomelamines** are formed by the polymerization of the alkylcyanamides, $CN.NHR'$, upon evaporating their solutions (obtained from the alkylthioureas on warming with mercuric oxide and water). They are crystalline bodies. When heated with hydrochloric acid they yield cyanuric esters and ammonium chloride (B. 18, 2784).

Trimethylisomelamine, $C_3N_3H_3(N.CH_3)_3 + 3H_2O$, melts at 179° when anhydrous. It sublimes at about 100°. **Triethylisomelamine**, $C_3N_3H_3(N.C_2H_5)_3 + 4H_2O$, consists of very soluble needles. Consult Hofmann, B. 18, 3217, for the phenyl derivatives of the mixed melamines (also amide and imide bodies).

COMPLEX CYANAMIDES.

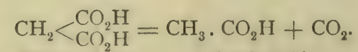
Melam, $C_6H_9N_{11} = [(NH_2)_2C_3N_3]_2NH$ (?), **Melem**, $C_6H_6N_{10} = [(NH_2)C_3N_3(NH)]_2$ (?), and **Mellon**, $C_6H_3N_9 = C_3N_3(NH)_3C_3N_3$ (?), are produced on igniting ammonium sulphocyanide. The first two are formed at 200°, and the latter at a red heat. They are amorphous white substances (B. 19, R. 340).

10. DIBASIC ACIDS, DICARBOXYLIC ACIDS.

A. PARAFFIN DICARBOXYLIC ACIDS, OXALIC ACID SERIES,

$C_nH_{2n-2}O_4$, $C_nH_{2n}(CO_2H)_2$.

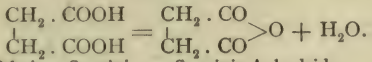
The acids of this series contain two carboxyl groups, and are therefore *dibasic*. They differ very markedly from each other on the application of heat, depending upon the position of the carboxyl groups. *Oxalic acid*, $CO_2H.CO_2H$, the first member of the series, breaks down on heating mostly into CO_2, CO and water, and in part into CO_2 and formic acid. The nature of the latter decomposition is characteristic of all those homologues of oxalic acid, in which the two carboxyls are attached to the same carbon atom—the β-dicarboxylic acids, *e. g.*, malonic acid, $CH_2(CO_2H)_2$. The latter acid and all *mono-* and *dialkylic* malonic acids decompose on heating at the ordinary pressure into acetic acid (also mono- and dialkylic acetic acids) with the elimination of CO_2. Malonic acid is the type of these acids:



$$CH_2{<}^{CO_2H}_{CO_2H} = CH_3.CO_2H + CO_2.$$

Malonic Acid   Acetic Acid.

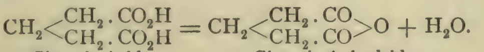
On the other hand, when the two carboxyl groups are attached to adjacent carbon atoms, as in ordinary or ethylene succinic acid, $CO_2H . CH_2 . CH_2 . CO_2H$, and in the alkylic ethylene succinic acids, then these γ-dicarboxylic acids, when heated, do not give up CO_2, but part with water and pass into *anhydrides*, which can also be prepared in other ways, whereas the anhydrides of the malonic acids are not known. Ethylene succinic acid is the type of these acids:



$$\begin{array}{l}CH_2 . COOH\\ |\\ CH_2 . COOH\end{array} = \begin{array}{l}CH_2 . CO\\ |\\ CH_2 . CO\end{array}\!\!>O + H_2O.$$

Ethylene Succinic Acid — Succinic Anhydride.

Glutaric acid, or normal pyrotartaric acid, $CO_2H . CH_2 . CH_2 . CH_2 . CO_2H$, in which the two carboxyl groups are attached to two carbon atoms, separated by a third, behaves in this manner. Like succinic acid, it yields a corresponding anhydride when it is heated. All acids, which can be regarded as alkylic glutaric acids, conduct themselves analogously:



$$CH_2\!<\!\begin{array}{l}CH_2 . CO_2H\\ CH_2 . CO_2H\end{array} = CH_2\!<\!\begin{array}{l}CH_2 . CO\\ CH_2 . CO\end{array}\!\!>O + H_2O.$$

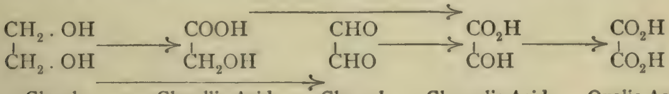
Glutaric Acid — Glutaric Anhydride.

When the carbon atoms, carrying the carboxyl groups, are separated by two carbon atoms from each other,—*e. g.*, adipic acid, $CO_2H . CH_2 . CH_2 . CH_2 . CH_2 . CO_2H$,—they do not influence one another on the application of heat.

Therefore, the numerous paraffin dicarboxylic acids are arranged in different groups, and after oxalic acid the malonic acid group, the succinic acid group, and the glutaric acid group will be discussed. Then will follow adipic acid, suberic acid, sebacic acid and others not belonging to any one of the three acid groups mentioned above.

Formation.—The most important general methods are—

(1) Oxidation of (*a*) diprimary glycols, (*b*) primary oxyaldehydes, (*c*) dialdehydes, (*a*) primary oxyacids, and (*e*) aldehyde acids (p. 363):

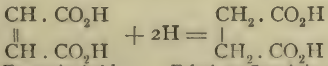


$$\begin{tikzcd}
\begin{array}{l}CH_2 . OH\\ |\\ CH_2 . OH\end{array} \arrow[r] \arrow[rr, bend right] & \begin{array}{l}COOH\\ |\\ CH_2OH\end{array} \arrow[rr, bend left] & \begin{array}{l}CHO\\ |\\ CHO\end{array} \arrow[r] & \begin{array}{l}CO_2H\\ |\\ COH\end{array} \arrow[r] & \begin{array}{l}CO_2H\\ |\\ CO_2H\end{array}
\end{tikzcd}$$

Glycol — Glycollic Acid — Glyoxal — Glyoxylic Acid — Oxalic Acid.

The dibasic acids are also formed when the fatty acids and the acids of the oleic acid series, as well as the fats, are oxidized by nitric acid. Certain hydrocarbons, C_nH_{2n}, have also been converted into dibasic acids by the action of potassium permanganate.

(2) By the reduction of unsaturated dicarboxylic acids:



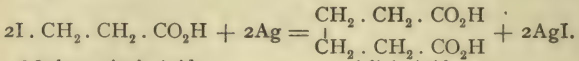
$$\begin{array}{l}CH . CO_2H\\ \|\\ CH . CO_2H\end{array} + 2H = \begin{array}{l}CH_2 . CO_2H\\ |\\ CH_2 . CO_2H\end{array}$$

Fumaric Acid — Ethylene Succinic Acid.

(3) When oxydicarboxylic acids and halogen dicarboxylic acids are reduced.

Nucleus-synthetic Methods of Formation.—These are very numerous with the dicarboxylic acids.

(4) When silver in powder form (B. **2**, 720) acts upon mono-iodo (or bromo-) fatty acids:

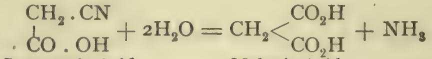


$$2I.CH_2.CH_2.CO_2H + 2Ag = \begin{array}{l} CH_2.CH_2.CO_2H \\ | \\ CH_2.CH_2.CO_2H \end{array} + 2AgI.$$

β-Iodopropionic Acid Adipic Acid.

Consult *trialkylic glutaric acids* for the abnormal course of this reaction when α-bromisobutyric acid is used.

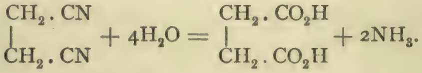
(5*a*) Conversion of monohalogen substituted fatty acids into cyan-derivatives, and boiling the latter with alkalies or acids (pp. 240 and 266):



$$\begin{array}{l} CH_2.CN \\ | \\ CO.OH \end{array} + 2H_2O = CH_2{<}\begin{array}{l} CO_2H \\ CO_2H \end{array} + NH_3$$

Cyanacetic Acid Malonic Acid.

(5*b*) Conversion of the halogen addition products of the alkylens, C_nH_{2n}, into cyanides and the saponification of the latter:

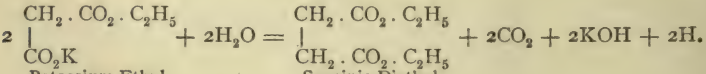


$$\begin{array}{l} CH_2.CN \\ | \\ CH_2.CN \end{array} + 4H_2O = \begin{array}{l} CH_2.CO_2H \\ | \\ CH_2.CO_2H \end{array} + 2NH_3.$$

Only the halogen products having their halogen atoms attached to two different carbon atoms can be converted into dicyanides.

(6) In the synthesis of the mono- and dialkylic malonic acids it is of the first importance to replace the hydrogen atoms of the CH_2 group of the malonic acid in its esters by alkyl groups, just as was done in the case of acetoacetic ester (p. 373). This reaction will be more fully developed in the malonic acid group (p. 439).

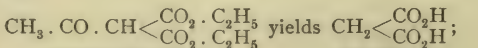
(7) By the electrolysis of concentrated solutions of alkyl ether potassium salts of the dicarboxylic acids (see electrolysis of the mono-carboxylic acids (pp. 76, 83, 243):



$$2\begin{array}{l} CH_2.CO_2.C_2H_5 \\ | \\ CO_2K \end{array} + 2H_2O = \begin{array}{l} CH_2.CO_2.C_2H_5 \\ | \\ CH_2.CO_2.C_2H_5 \end{array} + 2CO_2 + 2KOH + 2H.$$

Potassium Ethyl Malonate Succinic Diethyl Ester.

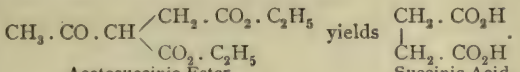
(8) A very general method for the synthesis of dibasic acids is founded upon the transposition of acetoacetic esters. Acid residues are introduced into the latter and the products decomposed by concentrated alkali solutions (p. 375). Thus, from acetomalonic ester we get malonic acid:



$$CH_3.CO.CH{<}\begin{array}{l} CO_2.C_2H_5 \\ CO_2.C_2H_5 \end{array} \text{ yields } CH_2{<}\begin{array}{l} CO_2H \\ CO_2H \end{array};$$

Acetomalonic Ester Malonic Acid.

and from acetosuccinic ester, succinic acid:

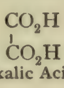


$$CH_3.CO.CH\begin{cases}CH_2.CO_2.C_2H_5\\CO_2.C_2H_5\end{cases} \text{ yields } \begin{array}{l}CH_2.CO_2H\\|\\CH_2.CO_2H\end{array}.$$

Acetosuccinic Ester — Succinic Acid.

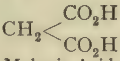
(9) Tricarboxylic acids, containing two carboxyl groups attached to the same C-atom, split off CO_2 and yield the dibasic acid. Ethane tricarboxylic acid yields succinic acid.

Isomerism.—The possible structural isomerides of the dicarboxylic acids depend upon whether the two COOH groups are attached to two different carbon atoms or to a single carbon atom. Isomerides of the first two members of the series—

(1) 

$$\begin{array}{l}CO_2H\\|\\CO_2H\end{array}$$

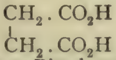
Oxalic Acid

and (2) 

$$CH_2<\begin{array}{l}CO_2H\\CO_2H\end{array}$$

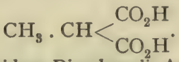
Malonic Acid

are not possible. For the third member two structural cases exist:

(3) 

$$\begin{array}{l}CH_2.CO_2H\\|\\CH_2.CO_2H\end{array}$$

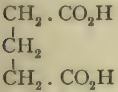
Ethylene Dicarboxylic Acid, Succinic Acid

and 

$$CH_3.CH<\begin{array}{l}CO_2H\\CO_2H\end{array}.$$

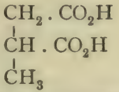
Ethidene Dicarboxylic Acid, Isosuccinic Acid.

There are four possible isomerides with the formula $C_3H_6<\begin{array}{l}CO_2H\\CO_2H\end{array}$, etc.; all are known:

(4) 

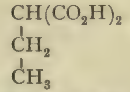
$$\begin{array}{l}CH_2.CO_2H\\|\\CH_2\\|\\CH_2.CO_2H\end{array}$$

Glutaric Acid, n-Pyrotartaric Acid



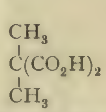
$$\begin{array}{l}CH_2.CO_2H\\|\\CH.CO_2H\\|\\CH_3\end{array}$$

Ord. Pyrotartaric Acid



$$\begin{array}{l}CH(CO_2H)_2\\|\\CH_2\\|\\CH_3\end{array}$$

Ethyl malonic Acid



$$\begin{array}{l}CH_3\\|\\C(CO_2H)_2\\|\\CH_3\end{array}$$

Dimethyl malonic Acid.

(5) The fifth member of the series, the acid $C_4H_8(CO_2H)_2$, has nine possible isomerides; all are known:

(*a*) Adipic acid—$CO_2H[CH_2]_4CO_2H$.

(*b*) α- and β-Methyl glutaric acid.

(*c*) Sym. and unsym. dimethyl succinic acid, ethyl succinic acid.

(*d*) Propyl-, isopropyl-, and methyl-ethyl malonic acids.

(6) There are twenty-four imaginable isomerides of the sixth member—the acids $C_5H_{10}(CO_2H)_2$ (A. **292**, 134).

Nomenclature (p. 57).—While the names of the older dicarboxylic acids—*e. g.*, oxalic, malonic, succinic, etc.—recall the occurrence or the methods of making these acids, the names of those acids which have been synthetically prepared from malonic esters are derived from malonic acid, *e. g.*, *methyl malonic acid*, *dimethyl malonic acid*. The names of the *alkyl-ethylene succinic acids*, etc., have been derived from ethylene succinic acid.

The "Geneva names" are deduced, like those for the mono-carboxylic acids, from the corresponding hydrocarbons; oxalic acid =

[Ethan-diacid]; malonic acid = [Propan-diacid]; ethylene succinic acid = [Butan-diacid]. The bivalent residues linked to the two hydroxyls are called the *radicals* of the dicarboxylic acids—*e. g.*, $CO.CO$, *oxalyl;* $CO.CH_2.CO$, *malonyl*, and $CO.CH_2.CH_2.CO$, *succinyl.* The *melting points* of the normal dicarboxylic acids exhibit great regularity. The members containing an even number of carbon atoms melt higher than those with an odd number (Baeyer, p. 62).

Derivatives of the Dicarboxylic Acids.—It has been indicated in connection with the monocarboxylic acids (p. 223) what derivatives of an acid can be obtained by a change in the carboxyl group. As might well be expected, the derivatives of the dicarboxylic acids are exceedingly more numerous, because not only the one group, but both carboxyls can take part in the reaction. The *heterocyclic derivatives* of the ethylene succinic and glutaric acid groups are particularly noteworthy. They are the *anhydrides* (p. 429) and the *acid imides, e. g., succinimide,* $\begin{matrix}CH_2.CO\\ |\\ CH_2.CO\end{matrix}>NH$, and *glutarimide,* $CH_2<\begin{matrix}CH_2.CO\\ CH_2.CO\end{matrix}>NH$. They have been previously mentioned.

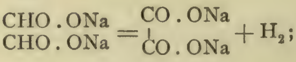
OXALIC ACID AND ITS DERIVATIVES.

(1) **Oxalic Acid,** [Ethan-diacid], $C_2O_4H_2$ (*Acidum oxalicum*), occurs in many plants, chiefly as potassium salt in the different varieties of *Oxalis* and *Rumex*. The calcium salt is often found crystallized in plant cells; it constitutes the chief ingredient of certain calculi. The acid may be prepared artificially (1) by oxidizing many carbon compounds, such as sugar, starch and others, with nitric acid.

Frequent mention has been made of its formation in the oxidation of glycol, glyoxal, glycollic acid and glyoxalic acid (pp. 295, 429).

(2) From cellulose: by fusing sawdust with caustic potash in iron pans at 200–220°. The fusion is extracted with water, precipitated as calcium oxalate, and this then decomposed by sulphuric acid (technical method).

(3) It is formed synthetically by (*a*) rapidly heating sodium formate above 440° (B. **15**, 4507):



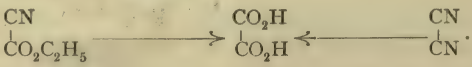
$$\begin{matrix}CHO.ONa\\ CHO.ONa\end{matrix} = \begin{matrix}CO.ONa\\ |\\ CO.ONa\end{matrix} + H_2;$$

by (*b*) oxidizing formic acid with nitric acid (B. **17**, 9).

(4) By conducting *carbon dioxide* over metallic sodium heated to 350–360° (A. **146**, 140):

$$2CO_2 + Na_2 = C_2O_4Na_2.$$

(5) Upon treating their *nitriles*, cyancarbonic ester and dicyanogen, with hydrochloric acid or water:



$$\begin{matrix}CN\\ |\\ CO_2C_2H_5\end{matrix} \longrightarrow \begin{matrix}CO_2H\\ |\\ CO_2H\end{matrix} \longleftarrow \begin{matrix}CN\\ |\\ CN\end{matrix}.$$

History.—In the very beginning of the seventeenth century salt of sorrel was known, and was considered to be a variety of argol. Wiegleb (1778) recognized the peculiarity of the acid contained in it. Scheele had obtained the free oxalic acid as early as 1776 upon oxidizing sugar with nitric acid, and showed in 1784 that it was identical with the acid of the salt of sorrel. Gay-Lussac (1829) discovered that oxalic acid was formed by fusing cellulose, sawdust, sugar, etc., with caustic potash. This process was introduced into practical manufacture in 1856 by Dale.

Constitution.—Free oxalic acid crystallizes with two molecules of water of crystallization. The crystallized acid is probably *ortho-oxalic acid*, $C(OH)_3 . C(OH)_3$ (p. 224). Ortho-esters of the acid $C_2(OR')_6$ are not known, but esters do exist, which are derived from the non-isolated *half-ortho-oxalic acid*, $C(OH)_3 . CO_2H$.

Properties and Transformations.—Oxalic acid crystallizes in monoclinic prisms, which effloresce at 20° in dry air. Large quantities of the acid, introduced into the system, are poisonous. It is soluble in 9 parts of water of medium temperature, and quite easily in alcohol. The hydrated acid melts at 101° if rapidly heated, and the anhydrous at 189° (B. **21**, 1901). Anhydrous oxalic acid crystallizes from concentrated sulphuric and nitric acid (B. **27**, R. 80), and will serve as a condensation agent for the splitting off of water (B. **17**, 1078). When carefully heated to 150° the anhydrous acid sublimes undecomposed. (1) Rapidly heated it decomposes into formic acid and carbon dioxide and also into CO_2, CO and water:

$$C_2H_2O_4 = CH_2O_2 + CO_2 ; \; C_2H_4O_2 = CO_2 + CO + H_2O.$$

(2) An aqueous oxalic acid solution under the influence of light decomposes into CO_2, H_2O, and with sufficient oxygen access, H_2O_2 (B. **27**, R. 496).

(3) Oxalic acid decomposes into carbonate and hydrogen by fusion with alkalies or soda-lime:

$$C_2O_4K_2 + 2KOH = 2CO_3K_2 + H_2.$$

(4) Heated with concentrated sulphuric acid it yields carbon monoxide, dioxide and water.

(5) Nascent hydrogen (Zn and H_2SO_4) converts it into glycollic acid.

(6) Concentrated nitric acid slowly oxidizes oxalic acid to CO_2 and water. However, permanganate of potash in acid solution rapidly oxidizes it. This reaction is used in volumetric analysis.

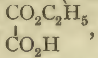
(7) PCl_5 changes oxalic acid to $POCl_3$, CO_2, CO, and 2HCl. It has also been possible to replace 2Cl by O in certain organic dichlorides upon using anhydrous oxalic acid (p. 446). $SbCl_5$, however, and oxalic acid yield the compound $(COOSbCl_4)_2$ (A. **239**, 285 ; **253**, 112).

The *oxalates*, excepting those with the alkali metals, are almost insoluble in water.

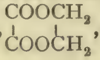
The *neutral potassium salt*, $C_2O_4K_2 + H_2O$, is very soluble in water. The *acid salt*, C_2O_4HK, dissolves with more difficulty, and occurs in the juices of plants (of *Oxalis* and *Rumex*). *Potassium quadroxalate*, $C_2O_4KH . C_2O_4H_2 + 2H_2O$.

Neutral Ammonium Oxalate, $C_2O_4(NH_4)_2 + H_2O$, consists of shining, rhombic prisms, which occur in *left* and *right-hemihedral crystals* (B. **18**, 1394). The *calcium oxalate*, $C_2O_4Ca + H_2O$, is insoluble in acetic acid, and serves for the detection of calcium and of oxalic acid, both of which are determined quantitatively in this form. The *silver salt*, $C_2O_4Ag_2$, explodes when quickly heated.

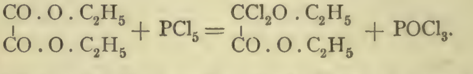
Oxalic Esters.—The acid and neutral esters of oxalic acid are formed simultaneously when anhydrous oxalic acid is heated with alcohols. They are separated by distillation under reduced pressure (Anschütz, A. **254**, 1).

Free Ethyl Oxalic Acid,  $\begin{array}{c}CO_2C_2H_5\\ |\\ CO_2H\end{array}$, boils undecomposed at 117° under 15 mm. pressure. Its sp. gr. at 20° equals 1.2175. *Norm. Propyl Oxalic Acid*, $CO_2 . C_3H_7 . CO_2H$, boils at 118° (13 mm.). Preserved in sealed tubes, the alkylic oxalic acids decompose into anhydrous oxalic acid, and the neutral esters. Distilled at the ordinary temperature, they break down mainly into oxalic ester, CO_2, CO and H_2O, and in part to CO_2 and formic esters.

Oxalic Methyl Ester, $C_2O_2(O . CH_3)_2$, melts at 54° and distils at 163°.

Oxalic Ethyl Ester boils at 186°, and is formed upon heating oxomalonic ester (B. **27**, 1304). See p. 385 for its conversion into carbonic ester. Oxalic ester, under the influence of sodium ethylate, condenses with acetic ester to oxalacetic ester, $CO_2C_2H_5 . CO . CH_2 . CO_2 . C_2H_5$, and with acetone to acetone oxalic ester (compare *chelidonic acid*). Zinc and alkyl iodides convert the oxalic ester into dialkyl oxalic esters (p. 33). *Ethylene Oxalic Ester,*  $\begin{array}{cc}COOCH_2 & \\ | \quad | & \\ COOCH_2 & \end{array}$, melts at 143° and boils at 197° (9 mm.) (B. **27**, 2941).

Half-ortho-oxalic Acid Derivatives.—*Dichloroxalic Esters:* When PCl_5 acts upon the neutral oxalic esters, one of the doubly-linked oxygen atoms is replaced by 2Cl atoms:



$$\begin{array}{c}CO . O . C_2H_5\\ |\\ CO . O . C_2H_5\end{array} + PCl_5 = \begin{array}{c}CCl_2O . C_2H_5\\ |\\ CO . O . C_2H_5\end{array} + POCl_3.$$

These products are called dichloroxalic esters (B. **28**, 61 Anm.). When fractionated under greatly reduced pressure, they can be separated from unaltered oxalic ester. Distilled at the ordinary pressure, these esters decompose into alkyl chlorides and alkylic oxalic acid chlorides (see below).

Dimethyl Dichloroxalic Ester, $CCl_2(OCH_3) . CO_2CH_3$, boils at 72° (12 mm.); its sp. gr. is 1.3591 (20°). *Diethyl Dichloroxalic Ester* boils at 85° (10 mm.). *Di-n-Propyl Dichloroxalic Ester* boils at 107° (10 mm.).

Half-ortho-oxalic Esters are produced by the transposition of dichloroxalic esters with sodium alcoholates in ether:

$$CO_2C_2H_5 . CCl_2 . O . C_2H_5 + 2C_2H_5ONa = CO_2C_2H_5 . C(O . C_2H_5)_3 + 2NaCl.$$

Tetramethyl Oxalic Ester, $C(OCH_3)_3 . CO . OCH_3$, boils at 76° (12 mm.); its sp. gr. is 1.1312. *Tetraethyl Oxalic Ester* boils at 98° (12 mm.) (A. **254**, 31).

The anhydride of oxalic acid is not known. In attempting to prepare it CO_2 and CO are produced. However, the chlorides of the alkylic oxalic acids, and probably oxalyl chloride, are known.

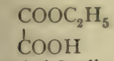
Chlorides of Alkylic Oxalic Acid are obtained by the action of $POCl_3$ upon potassium alkylic oxalates. It is most practically prepared by boiling dichloroxalic esters under the ordinary pressure until the evolution of the alkyl chlorides ceases (A. **254**, 26). They show the reactions of an acid chloride (p. 257). With benzene hydrocarbons and Al_2Cl_6 they yield phenyl glyoxylic esters and their homologues (B. **14**, 1689; **29**, R. **511**, 546).

Methyl Oxalic Chloride, $COCl . CO_2 CH_3$, boils at 118–120°; sp. gr. 1.3316 (20°). *Ethyl Oxalic Chloride*, $COCl . CO_2 . C_2H_5$, boils at 135°; sp. gr. 1.2223.

n-*Propyl Oxalic Chloride* boils at 153°. *Isobutyl Oxalic Chloride* boils at 164°. *Amyl Oxalic Chloride* boils at 184°. These are liquids with a penetrating odor. *Oxalyl Chloride*, $C_2O_2Cl_2$(?), boils at 70°. It has not been obtained free from $POCl_3$. It is said to be formed when two molecules of phosphorus oxychloride act upon $(CO . OC_2H_5)_2$ (B. **25**, R. 110).

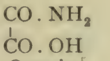
AMIDES OF OXALIC ACID.

Oxalic acid yields two amides: *oxamic acid*, corresponding to ethyl oxalic acid, and *oxamide*, corresponding to oxalic ester. *Oximide* can be included with these:



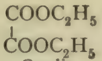
$$\begin{matrix}COOC_2H_5\\ |\\ COOH\end{matrix}$$

Ethyl Oxalic Acid



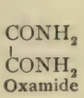
$$\begin{matrix}CO\,.\,NH_2\\ |\\ CO\,.\,OH\end{matrix}$$

Oxamic Acid



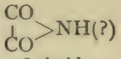
$$\begin{matrix}COOC_2H_5\\ |\\ COOC_2H_5\end{matrix}$$

Oxalic Ester



$$\begin{matrix}CONH_2\\ |\\ CONH_2\end{matrix}$$

Oxamide



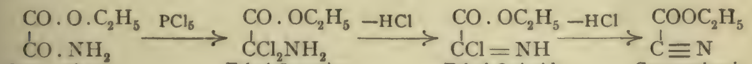
$$\begin{matrix}CO\\ |\\ CO\end{matrix}>NH(?)$$

Oximide.

Oxamic Acid, $C_2O_2<\substack{NH_2\\OH}$, melts at 210° with decomposition. Its ammonium salt (Balard, 1842) is produced by heating acid ammonium oxalate; by boiling oxamide with ammonia, and by boiling oxamæthane with ammonia (B. **19**, 3229; **22**, 1569). It is a crystalline powder, that dissolves with difficulty in cold water.

Its *esters* result from the action of alcoholic or dry ammonia upon the esters of oxalic acid:

Ethyl Oxamic Ester (Oxamæthane), $C_2O_2<\substack{NH_2\\O\,.\,C_2H_5}$, consists of shining, fatty-feeling leaflets. It melts at 114–115° (Boullay and Dumas, 1828). The behavior of oxamæthane toward PCl_5 is important theoretically, because at first it yields *oxamæthane chloride*, Ethyl Oxamine Chloride Ester, a derivative of half-ortho-oxalic acid. This splits off a molecule of HCl and becomes the ethyl ester of oximide chloride, and by the loss of a second molecule of HCl passes into cyancarbonic ester (Wallach, A. **184**, 1):



$$\begin{matrix}CO\,.\,O\,.\,C_2H_5\\ |\\ CO\,.\,NH_2\end{matrix}\xrightarrow{PCl_5}\begin{matrix}CO\,.\,OC_2H_5\\ |\\ CCl_2NH_2\end{matrix}\xrightarrow{-HCl}\begin{matrix}CO\,.\,OC_2H_5\\ |\\ CCl=NH\end{matrix}\xrightarrow{-HCl}\begin{matrix}COOC_2H_5\\ |\\ C\equiv N\end{matrix}$$

Oxamæthane — Ethyl Oxamine Chloride — Ethyl Oximide Chloride — Cyancarbonic Ester.

Oxamine Ortho-trimethyl Ether, $CONH_2\,.\,C(O\,.\,CH_3)_3$, melting at 115°, is formed on heating half-ortho-oxalic methyl ester with anhydrous methyl alcoholic ammonia.

Methyl Oxamic Acid, $CONH(CH_3)\,.\,CO_2H$, melts at 146°.

Ethyloxamic Acid, $C_2O_2<\substack{NH\,.\,C_2H_5\\OH}$, melts at 120°.

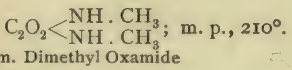
Ethyl Dietho-oxamic Ester, $C_2O_2<\substack{N(C_2H_5)_2\\O\,.\,C_2H_5}$ (Diethyloxamæthane), boils at 254°. It is produced by the action of diethylamine upon oxalic esters. It regenerates diethylamine on distilling with potash. A method for separating the amines (p. 164) is based on this behavior.

Oxanilic Acid (see this).

Oxalimide, $\begin{matrix}CO\\ |\\ CO\end{matrix}>NH$ (?), is obtained from oxamic acid by the aid of PCl_5 or PCl_3O (B. **19**, 3229). The molecule is probably twice as large.

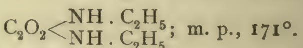
Oxamide, $C_2O_2(NH_2)_2$, separates as a white, crystalline powder, when neutral oxalic ester is shaken with aqueous ammonia (1817, Bauhof). It is insoluble in water and alcohol. It is also formed on heating ammonium oxalate (1830, Dumas; 1834, Liebig), and when water and a trace of aldehyde act on cyanogen, C_2N_2, or by the direct union of hydrocyanic acid and hydrogen peroxide ($2CNH + H_2O_2 = C_2O_2N_2H_4$). Oxamide is partially sublimed when heated, the greater part, however, being decomposed. When heated to 200° with water, it is converted into ammonium oxalate. P_2O_5 converts it into dicyanogen.

The *substituted oxamides* containing alcohol radicals are produced by the action of the primary amines upon the oxalyl esters—*e. g.*:



$$C_2O_2{<}\begin{matrix}NH\,.\,CH_3\\ NH\,.\,CH_3\end{matrix};\ \text{m. p., }210^\circ.$$

Sym. Dimethyl Oxamide



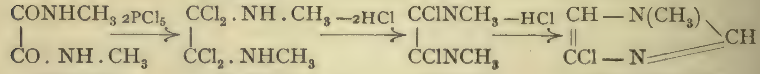
$$C_2O_2{<}\begin{matrix}NH\,.\,C_2H_5\\ NH\,.\,C_2H_5\end{matrix};\ \text{m. p., }171^\circ.$$

Sym. Diethyl Oxamide.

Tetramethyl Oxamide, $[CON(CH_3)_2]_2$, melting at 80°, is obtained from dimethyl urea chloride by the action of ammonia (B. **28**, R. 234).

See also *Oxanilide*, later.

PCl_5 converts these alkylic oxamides into amide chlorides, which lose 3HCl and pass into *glyoxaline derivatives* (Wallach, A. **184**, 33; Japp, B. **15**, 2420): thus *diethyl oxamide* yields chloroxalmethylin, and diethyl oximide yields *chloroxalethylin*:



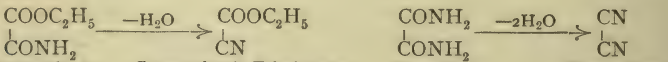
Dimethyl Oxamide — Dimethyl Oxamide Tetrachloride — Dimethyl Oximide Dichloride — Chloroxalmethylin.

Hydrazide and Hydroxyamide of Oxalic Acid, Oxalhydrazide, $\begin{matrix}CONH\,.\,NH_2\\ |\\ CO\,.\,NH\,.\,NH_2\end{matrix}$, turns brown and decomposes at 235°. It is produced by the action of the hydrazine hydrate upon oxalic ester (J. pr. Ch. [2] **51**, 194).

Hydroxyl Oxamide, $\begin{matrix}CONH\,.\,OH\\ |\\ CONH_2\end{matrix}$, melting at 159°, is obtained from oxamæthane and hydroxylamine. *Acetoxyloxamide*, $NH_2\,.\,CO\,.\,CO\,.\,NHO\,.\,CO\,.\,CH_3$, melts at 173°. When heated with acetic anhydride to 110°, it is decomposed into cyanuric acid (p. **419**), and acetic acid (A. **288**, 314).

NITRILES OF OXALIC ACID.

Two nitriles correspond to each dicarboxylic acid: a nitrilic acid, or a half-nitrile, and a dinitrile. The nitrilic acid of oxalic acid is *cyancarbonic*, *cyanformic*, or *oxalnitrilic acid*. It is only known in its esters. Dicyanogen is the dinitrile of oxalic acid. The kinship of these nitriles to oxalic acid is manifested by their formation from the oxamic esters and oxamide through the elimination of water, and their conversion into oxalic acid by the absorption of water and the splitting-off of ammonia:



$$\begin{matrix}COOC_2H_5\\ |\\ CONH_2\end{matrix}\xrightarrow{-H_2O}\begin{matrix}COOC_2H_5\\ |\\ CN\end{matrix}\qquad\begin{matrix}CONH_2\\ |\\ CONH_2\end{matrix}\xrightarrow{-2H_2O}\begin{matrix}CN\\ |\\ CN\end{matrix}$$

Oxamæthane — Cyancarbonic Ethyl Ester — Oxamide — Dicyanogen.

Cyancarbonic Esters, Cyanformic Esters, Nitrilo-oxalic Esters, are produced in the distillation of oxamic esters with P_2O_5 or PCl_5 (p. 435), as well as from cyanimido-carbonic ether. *Cyancarbonic Methyl Ester*, $CN\,.\,CO_2\,.\,CH_3$, boils at 100°. *Cyancarbonic Ethyl Ester* boils at 115°. These are liquids with a penetrating odor.

They are insoluble in water, which slowly decomposes them into CO_2, prussic acid, and alcohols. Zinc and hydrochloric acid convert them into *glycocoll* (p. 354). Concentrated hydrochloric acid breaks them down into *oxalic acid*, ammonium chloride, and alcohols. Bromine or gaseous HCl at 100° transforms the ethyl ester into a polymeric, crystalline body, melting at 165°, and by the action of cold alkalies yielding salts of *paracyancarbonic acid—e.g.*, $(CN.CO_2K)n$.

Cyanorthoformic Ester, *Triethoxyacetonitrile*, *Ortho-oxalnitrilic Ethyl Ester*, $CN.C(OC_2H_5)_3$, boils at 160° (A. **229**, 178).

Trinitroacetonitrile, $CNC(NO_2)_3$, melts at 41.5° and explodes at 220° (see fulminuric acid, p. 238).

Dicyanogen, Oxalonitrile, [Ethan Dinitrile], NC . CN, is present in small quantity in the gases of the blast furnace. It was obtained in 1815 by Gay-Lussac by the ignition of mercury cyanide. The transposition proceeds more readily by the addition of mercuric chloride:

$$Hg(CN_2) = C_2N_2 + Hg. \quad Hg(CN)_2 + HgCl_2 = C_2N_2 + Hg_2Cl_2.$$

Silver and gold cyanides deport themselves similarly. Dicyanogen is most readily prepared from potassium cyanide. To this end the concentrated aqueous solution of 1 part KCN is gradually added to 2 parts cupric sulphate in 4 parts of water. Heat is then applied. At first a yellow precipitate of copper cyanide, $Cu(CN)_2$, is produced, but it immediately breaks up into cyanogen gas and cuprous cyanide, CuCN (B. **18**, R. 321):

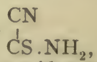
$$2SO_4Cu + 4CNK = Cu_2(CN)_2 + (CN)_2 + 2SO_4K_2.$$

Its preparation from ammonium oxalate and oxamide, through the agency of heat, is of theoretical interest. The same may be said of its formation upon passing the induction spark between carbon points in an atmosphere of nitrogen (1859, Morren).

Cyanogen is a colorless, peculiar-smelling, poisonous gas. It may be condensed to a mobile liquid by cold of —25°, or by a pressure of five atmospheres at ordinary temperatures. In this condition it has a sp. gr. 0.866, solidifies at —34° to a crystalline mass, and boils at —21°. It burns with a bluish-purple mantled flame. Water dissolves 4 volumes and alcohol 23 volumes of the gas.

On standing the solutions become dark and break down into ammonium oxalate and formate, hydrogen cyanide and urea, and at the same time a brown body, the so-called *azulmic acid*, $C_4H_5N_5O$, separates. With aqueous potash cyanogen yields potassium cyanide and isocyanate. In these reactions the molecule breaks down, and if a slight quantity of aldehyde be present in the aqueous solution, only oxamide results. Oxalic acid is produced in the presence of mineral acids, $C_2N_2 + 4H_2O = C_2O_4H_2 + 2NH_3$. Concentrated hydriodic acid converts it into glycocoll (p. 354).

On heating mercuric cyanide there remains a dark substance, *paracyanogen*, a polymeric modification, $(C_2N_2)n$. Strong ignition converts it again into cyanogen. It yields potassium cyanate with caustic potash.



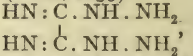
With hydrogen sulphide cyanogen yields *hydroflavic acid*, $C_2N_2 . H_2S = \begin{array}{l}CN\\ | \\ CS.NH_2\end{array}$, and *hydrorubianic acid*, $C_2N_2 . 2H_2S$. These two compounds may be considered thioamides.

Hydrorubianic acid dissolves with difficulty in chloroform, from which hydroflavic acid crystallizes in yellow, transparent, flat needles, melting with decomposition at 87–89° (A. **254**, 262). Hydrorubianic acid consists of yellow-red needles. Primary bases replace the amido-groups by alkylic amido-groups (A. **262**, 354). It combines with the aldehydes with the elimination of water (B. **24**, 1027).

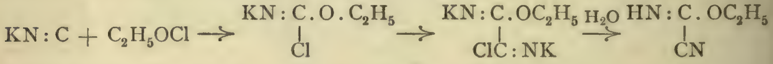
Diamido-oxal ethers result from the action of ammonia upon dichloroxalic esters. They have not yet been obtained in a pure condition. Aniline and dichloroxalether in cold ethereal solution yield *Dianilido-oxal ether*, $CO_2C_2H_5C(NHC_6H_5)_2OC_2H_5$, a thick liquid soluble in ether. At 0° hydrochloric acid precipitates from this ethereal solution the dichlorhydrate, $CO_2C_2H_5C(NHC_6H_5 . HCl)_2O . C_2H_5$. Mixed diamido-ethers can be obtained by allowing anhydrous ammonia gas to act upon a cooled, ethereal solution of monophenylimido-oxalic acid dimethyl ether. In this way *Amido-anilido-oxalic methyl ester*, $CO_2CH_3 . C(NH_2)(NHC_6H_5)O . CH_3$, is obtained. It melts at 215°. *Imido-oxalic Ethers:* Monoimido-oxalic Ether, $CO_2C_2H_5 . C(:NH)\text{-}OC_2H_5$, boiling at 73° (18 mm.), results from the action of a calculated amount of $\frac{1}{10}$ n-hydrochloric acid upon di imido-oxalic ether (A. **288**, 289). *Phenyl-imido-oxal-methyl Ether*, $CO_2CH_3 . C(=N . C_6H_5)O . CH_3$.

Di-imido-oxal-Ether, $C_2H_5O . (NH)C - C(NH) . OC_2H_5$, melts at 25° and boils at 170°. Its hydrochloride is obtained on conducting HCl into an alcoholic solution of cyanogen (B. **11**, 1418) (compare pp. 232, 269).

Oxalamidine, $NH_2(NH)C - C(NH)NH_2$, results from the action of alcoholic ammonia upon the hydrochloride of oximido-ether (B. **16**, 1655).

Carbohydrazidine, Oxaldi-imide-dihydrazide,  $\begin{array}{l}HN:C.NH.NH_2\\ \quad\;\, | \\ HN:C.NH.NH_2\end{array}$, white, flat needles, which assume a reddish-brown color on heating and do not melt at 250°. It results from the union of cyanogen with hydrazine. *Dibenzal carbohydrazidine* melts at 218° (J. pr. Ch. [2] **50**, 253).

Cyanimido-carbonic Ether, Nitrilo-oxal-imido-ether, $CN . C(:NH)O . C_2H_5$, boiling at 50° (30 mm.), is obtained from chlorcyanogen or bromcyanogen, water, alcohol, and potassium cyanide, as well as from aqueous potassium cyanide and ethyl hypochlorite (p. 148), when the following intermediate products probably arise:



$$KN:C + C_2H_5OCl \longrightarrow \begin{array}{c}KN:C.O.C_2H_5\\ |\\ Cl\end{array} \longrightarrow \begin{array}{c}KN:C.OC_2H_5\\ |\\ ClC:NK\end{array} \xrightarrow{H_2O} \begin{array}{c}HN:C.OC_2H_5\\ |\\ CN\end{array}$$

This reaction certainly favors the formula K . N : C for potassium cyanide, because it can not be clearly understood with the formula KCN (A. **287**, 273). Cyan-imido-carbonic ether is a yellowish oil, with a sweet and at the same time penetrating odor.

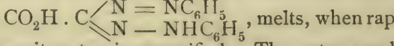
Chlorethylimidoformyl Cyanide, Nitril-oxalo-ethyl-imide chloride, $CN . C(:NC_2H_5)Cl$, from chlorcyanogen and ethyl isocyanide (A. **287**, 302), boils at 126°.

Oxaldihydroxamic Acid, $[C:(NOH)OH]_2$, melting at 165°, results from oxalic ester and hydroxylamine (B. **27**, 799, 1105).

Oxaldiamidoxime, $[C(N . OH)NH_2]_2$, melts with decomposition at 196°. It is formed when NH_2OH acts (1) upon cyanogen (B. **22**, 1931), (2) upon cyananiline (B. **24**, 801), (3) upon hydrorubianic acid (B. **22**, 2306). Its *dibenzoyl derivative* melts at 222° (B. **27**, R. 736).

Chloro-oximido-acetic Ester, Ethoxalo-oxime Chloride, $CO_2C_2H_5 . C(:NOH)Cl$, melting at 80°, is obtained from chloracetoacetic ester by means of fuming nitric acid, and when concentrated hydrochloric acid acts upon nitrol-acetic ester (B. **28**, 1217).

Nitrol-acetic Ester, Ethoxal-nitrolic Acid, $CO_2C_2H_5 . C(:NOH) . NO_2$, from iso-nitroso-acetoacetic ester and nitric acid of sp. gr. 1.2 (B. **28**, 1217), melts at 69°.

Formazyl Carbonic Acid,  $CO_2H . C\begin{array}{l}\diagup N = NC_6H_5\\ \diagdown\!\!\diagdown N - NHC_6H_5\end{array}$, melts, when rapidly heated, at 162°. It is produced when its ester is saponified. The ester results from the action of diazo-benzene chloride (1) upon the hydrazone of mesoxalic ester, (2) upon sodium malonic ester, and (3) upon acetoacetic ester. Oxalic acid breaks down into formic acid and CO_2, and formazyl carbonic acid decomposes into formazyl hydride (p. 233) and CO_2 (B. **25**, 3175, 3201).

Parabanic acid and oxaluric acid are ureïdes of oxalic acid. They will be considered together with the derivatives of uric acid (see these).

THE MALONIC ACID GROUP.

Malonic Acid [*Propan Diacid*], $CH_2(CO_2H)_2$, melts at 132°. It occurs as calcium salt in sugar-beets. (1) The acid was discovered in 1858, by Dessaignes, on oxidizing malic acid, $CO_2H.CH(OH).CH_2-CO_2H$, with potassium bichromate (hence the name, from *malum*, apple) and quercitol with potassium permanganate (B. **29**, 1764). It is also (2) produced in the oxidation of hydracrylic acid, and (3) of *propylene* and *allylene* by means of $KMnO_4$. (4) Kolbe and Hugo Müller obtained it almost simultaneously (1864) by the conversion of chloracetic acid into cyanacetic acid, the nitrile acid of malonic acid, and then saponifying the latter with caustic potash. (5) By the decomposition of barbituric acid or its malonyl urea (see this). (6) Malonic ester and CO are formed in the distillation of oxalacetic ester (see this) under the ordinary pressure (B. **27**, 795).

Preparation.—One hundred grams of chloracetic acid, dissolved in 200 grams of water, are neutralized with sodium carbonate (110 grams), and to this 75 grams of pure, pulverized potassium cyanide are added, and the whole carefully heated, after solution, upon a water-bath. The cyanide produced is saponified either by concentrated hydrochloric acid or potassium hydroxide (B. **13**, 1358; A. **204**, 225). To obtain the malonic ester directly, evaporate the cyanide solution, cover the residue with absolute alcohol and lead HCl gas into it (A. **218**, 131), or treat it with sulphuric acid and alcohol (C. 1897, I, 282).

Properties.—Malonic acid crystallizes in triclinic plates. It is easily soluble in water and alcohol. Above its melting point it decomposes into acetic acid and carbon dioxide. Bromine in aqueous solution converts it into tribromacetic acid and CO_2, while iodic acid changes it to di- and tri-iodoacetic acid (p. 275) and CO_2.

Salts.—Barium salt, $(C_3H_2O_4)Ba + 2H_2O$. The *calcium salt*, $C_3H_2O_4Ca) + 2H_2O$, dissolves with difficulty in cold water. The *silver salt*, $C_3H_2Ag_2O_4$, is a white, crystalline compound.

Ester.—Potassium ethyl malonate, from the ester and caustic potash, yields ethylene succinic ester when it is electrolyzed (pp. 430, 443).

The *neutral malonic esters* are made by treating potassium cyanacetate or malonic acid with alcohols and hydrochloric acid. These compounds are of the first importance in the synthesis of the polycarboxylic acids, because of the replaceability of the hydrogen atoms of the CH_2-group by sodium.

History.—This property was first observed in 1874 by van t'Hoff, Sr. (B. **7**, 1383), and the possibility of obtaining the malonic acid homologues, by means of it, was indicated. The comprehensive, exhaustive experiments begun in 1879 by Conrad first demonstrated that malonic esters were almost as valuable as the acetoacetic esters in carrying out certain synthetic reactions (pp. 371, 376) (A. **204**, 121).

The *methyl ester*, $CH_2(CO_2 . CH_3)_2$, boils at 181°. The *ethyl ester* boils at 198°; its specific gravity at 18° is 1.068. By the action of sodium ethylate upon it the Na-compounds, $CHNa(CO_2 . C_2H_5)_2$ and $CNa_2(CO_2 . C_2H_5)_2$ (B. **17**, 2783; **24**, 2889 Anm.), result. Malonic ester is *not* soluble in aqueous alkalies. Iodine converts both sod-malonic esters into ethane and ethylene tetracarboxylic esters. Sodium malonic ester, when electrolyzed, yields ethane tetracarboxylic ester (B. **28**, R. 450). Alkyl haloids convert the sodium malonic esters into esters of malonic acid homologues (B. **28**, 2616). The malonic esters and diazobenzene chloride yield phenylhydrazone mesoxalic esters (see these). Upon heating sodium malonic ester to 145° a condensation of 3 molecules occurs, with a splitting-off of 3 molecules of alcohol, and there remains the ester of trisod-phloroglucin tricarboxylic acid (a derivative of benzene) (B. **18**, 3458):

$$3CHNa(CO_2C_2H_5)_2 = C_6O_3Na_3(CO_2 . C_2H_5)_3 + 3C_2H_5OH.$$

The malonic esters and diazobenzene chloride yield phenylhydrazone-mesoxalic esters (see these).

Malonic Anhydride, $CH_2<\substack{CO \\ CO}>O$, is not known (comp. p. 428).

Malonic Acid Chlorides: Chloride of Ethyl Malonic Ester, $CO_2 . C_2H_5 . CH_2COCl$, obtained from potassium ethyl malonate by the action of PCl_5, boils at 170–180° (B. **25**, 1504).

Malonyl Chloride, $CH_2(COCl)_2$. produced when $SOCl_2$ acts upon malonic acid (B. **24**, R. 322), boils at 58° (27 mm.).

Malonamic Ethyl Ester, $CO_2C_2H_5 . CH_2 . CO . NH_2$, melting at 50°, is formed upon heating the hydrochloride of mono-imido-malonic ester (B. **28**, 479). *Malonamide*, $CH_2(CONH_2)_2$, melts at 170° (B. **17**, 133). *Imidomalonamide*, $NH_2 . CO . CH_2 . C(:NH)NH_2$. *Malonhydrazide*, $CH_2(CO . NH . NH_2)_2$, melts at 152° (J. pr. Ch. [2] **51**, 187).

Nitriles of Malonic Acid: Cyanacetic Acid, Nitrilomalonic Acid, half nitrile of malonic acid, $CN . CH_2 . CO_2H$ (p. 439), melts at 70° (B. **27**, R. 262). It dissolves very readily in water, and at about 165° breaks down into CO_2 and acetonitrile (p. 268). *Cyanacetic Ethyl Ester*, $CN . CH_2 . CO_2 . C_2H_5$, boiling at 207°, forms sodium derivatives like malonic ester, by means of which the hydrogen of the CH_2-groups can be replaced by alkyls (B. **20**, R. 477) and acid radicals (B. **21**, R. 353). *Cyanacetamide*, $CN . CH_2 . CONH_2$, from the ester and ammonia, melts at 118°. *Cyanacethydrazide*, $CNCH_2CO . NHNH_2$, melts at 114° (J. pr. Ch. [2] **51**, 186).

Malononitrile, $CH_2<\substack{CN \\ CN}$, methylene cyanide, is obtained by distilling cyanacetamide with P_2O_5 (C. 1897, I, 32). It is soluble in water. Silver nitrate precipitates $CAg_2(CN)_2$ from the aqueous solution (B. **19**, R. 485). Hydrazine and malononitrile yield diamidopyrazole, $C_3N_2H_2(NH_2)_2$ (B. **27**, 690). See also cyanoform. *Methenylamidoxime-acetic Acid*, $NH_2(HON) : C . CH_2 . CO_2H$, melts at 144° (B. **27**, R. 261). *Nitrilomalonimidoxime, Cyanethenylamidoxime*, $CN . CH_2 . C(:N . OH)NH_2$, melts at 124–127°. *Malondihydroxamic Acid*, $CH_2[C(:NOH)OH]_2$, melts at 154° (B. **27**, 803). *Malondiamidoxime*, $CH_2 . [C(:N . OH)NH_2]_2$, melts at 163–167° (B. **29**, 1168).

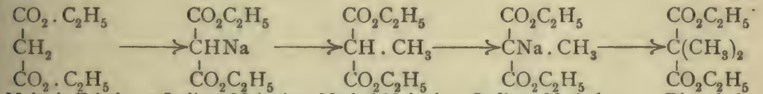
The ureïdes of malonic acid will be treated later in connection with uric acid (see this).

Halogen Malonic Acids are produced when chlorine and bromine act upon malonic acid and malonic esters (B. **21**, 1356).

Chlormalonic Ester, $CHCl(CO_2 . C_2H_5)_2$, boils at 222°. *Brom-malonic Ester* boils with decomposition at 235° (B. **24**, 2993, 2997; compare also *tartronic acid*). *Brom-malononitrile* melts at 65° (C. 1897, I, 32). *Dichlormalonic Ester*, $CCl_2(CO_2 . C_2H_5)_2$, boils at 231–234°. *Dibrom-malonic Acid* melts at 126°. *Dibrom-malononitrile* melts at 109° (C. 1897, I, 32). *Dibrom-malonic Ester* boils at 145° to 155°

(25 mm.) (B. **24**, 3001; compare also mesoxalic acid). The mono- and dichlor- or brom-malonic acids link malonic acid to *tartronic* (p. 485) and *mesoxalic acids* (p. 497).

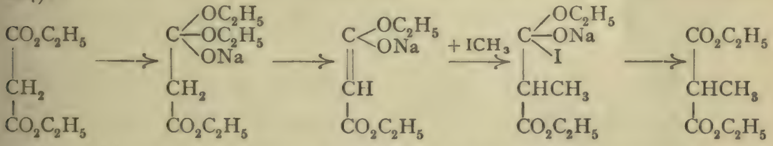
Alkylic Malonic Acids.—The general methods suitable for the preparation of alkylic malonic acids are (1) reaction 5*a* (p. 430), conversion of *a*-halogen fatty acids into *a*-cyan-fatty acids—the half nitriles of the malonic acid homologues; and (2) reaction 6 (p. 430), the replacement of the hydrogen atoms of the CH_2 group in the malonic esters by alkyls. First, with the aid of sodium ethylate, mono-sodmalonic esters are made, which alkyl iodides convert into mono-alkylic malonic esters. These are further able to yield monosodium alkylic malonic esters, which alkylogens change to dialkylic malonic esters—*e. g.*:



$$\begin{array}{c}CO_2.C_2H_5\\|\\CH_2\\|\\CO_2.C_2H_5\end{array}\longrightarrow\begin{array}{c}CO_2C_2H_5\\|\\CHNa\\|\\CO_2C_2H_5\end{array}\longrightarrow\begin{array}{c}CO_2C_2H_5\\|\\CH.CH_3\\|\\CO_2C_2H_5\end{array}\longrightarrow\begin{array}{c}CO_2C_2H_5\\|\\CNa.CH_3\\|\\CO_2C_2H_5\end{array}\longrightarrow\begin{array}{c}CO_2C_2H_5\\|\\C(CH_3)_2\\|\\CO_2C_2H_5\end{array}$$

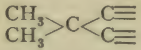
Malonic Ethyl Ester · Sodium Malonic Ester · Methyl Malonic Ester · Sodium Methyl Malonic Ester · Dimethyl Malonic Ester.

It has been previously mentioned under acetoacetic ester (p. 373) that the reaction consisted in the addition of sodium ethylate to the carboxethyl group, with the splitting-off of alcohol and the production of a double union, to which the alkylogen attached itself, and there then followed the elimination of a sodium halide (A. **280**, 264):



$$\begin{array}{c}CO_2C_2H_5\\|\\CH_2\\|\\CO_2C_2H_5\end{array}\longrightarrow\begin{array}{l}C\begin{cases}OC_2H_5\\OC_2H_5\\ONa\end{cases}\\|\\CH_2\\|\\CO_2C_2H_5\end{array}\longrightarrow\begin{array}{l}C<^{OC_2H_5}_{ONa}\\\|\\CH\\|\\CO_2C_2H_5\end{array}\xrightarrow{+ICH_3}\begin{array}{l}C\begin{cases}OC_2H_5\\ONa\\I\end{cases}\\|\\CHCH_3\\|\\CO_2C_2H_5\end{array}\longrightarrow\begin{array}{c}CO_2C_2H_5\\|\\CHCH_3\\|\\CO_2C_2H_5\end{array}$$

Some of these dialkylic malonic acids are formed when complex carbon derivatives are oxidized—*e. g.*, dimethyl malonic acid results from the oxidation of unsymmetrical dimethyl ethylene succinic acid, mesitonic acid, camphor, etc. The production of dimethyl malonic acid in this manner proves the presence, in these bodies, of the atomic grouping—



$$\begin{array}{c}CH_3\\CH_3\end{array}>C<\begin{array}{c}C\equiv\\C\equiv\end{array}$$

All mono- and dialkylic malonic acids, when exposed to heat, split off CO_2 and pass into mono- (B. 27, 1177) *and dialkylic acetic acids* (p. 428).

See Z. phys. Ch. **8**, 452, for the affinity magnitudes of the alkylic malonic acids. Consult B. **29**, 1864, upon the speed of saponification of the alkylic malonic esters.

Iso-succinic Acid, Ethidene Succinic Acid, Methyl Malonic Acid [Methyl propan di-acid], melts at 130° with decomposition. It is isomeric with ordinary succinic acid or ethylene succinic acid (p. 431), and is obtained (1) from *a*-chlor- and *a*-brom-propionic acids through the cyanide (B. **13**, 209), and (2) from sodium malonic ester and methyl iodide.

When ethidene bromide, $CH_3 . CHBr_2$, is heated with potassium cyanide and alkalies, we do not obtain ethidene succinic acid by the operation, but by molecular rearrangement, ordinary ethylene succinic acid.

The acid is more soluble than ordinary succinic acid in water. If heated above 130°, it breaks up into carbon dioxide and propionic acid (p. 246). The *ethyl ester* boils at 196°; the *methyl ester* at 179°.

α-Cyanpropionic Ester, $CH_3 . CH(CN)CO_2C_2H_5$, boils at 197–198°.

Bromisosuccinic Acid, $CH_3 . CBr(CO_2H)_2$, melts at 118–119° (B. **23**, R. 114).

Methyl Brom-malonic Ester boils at 115–118° (15 mm.) (B. **26**, 2356).

Ethyl Malonic Acid, $C_2H_5 . CH(CO_2H)_2$, melts at 111.5°. The *ethyl ester* boils at 200°. *Ethylbrommalonic Ester* boils at 125° (10 mm.) (B. **26**, 2357).

Dimethyl Malonic Acid, $(CH_3)_2C(CO_2H)_2$, melts at 117°; the *ethyl ester* boils at 195°. The *nitrile* melts at 32° and boils at 64° (22 mm.). Compare the 3d method of formation as given above. Both acids are isomeric with pyrotartaric acid and n-glutaric acid (see p. 431).

In the case of the subjoined alkylic malonic acids, the boiling points of the ethyl esters (inclosed in parentheses) are given, together with the melting points of the acids.

Propylmalonic Acid, $CH_3 . CH_2 . CH_2CH(CO_2H)_2$, melts at 96° (219–222°).

Isopropylmalonic Acid, $(CH_3)_2 . CH . CH(CO_2H)_2$, melts at 87° (213–214°).

Methyl-ethyl Malonic Acid, $CH_3(C_2H_5)C(CO_2H)_2$, melts at 118° (207–208°). These three acids are isomeric with adipic acid, methyl glutaric acid, ethyl and dimethyl succinic acids (see p. 431).

Norm. Butylmalonic Acid, $CH_3(CH_2)_3 . CH(CO_2H)_2$, melts at 101.5°. *Isobutyl-Malonic Acid* melts at 107° (225°). Sec. *Butyl Malonic Acid*, $CH_3(C_2H_5)CH . CH(CO_2H)_2$, melts at 76° (233–234°). *Propylmethyl Malonic Acid*, $CH_3(CH_3 . CH_2 . CH_2)C(CO_2H)_2$, melts at 106–107° (220–223°). *Isopropylmethyl Malonic Acid* melts at 124° (221°). *Diethylmalonic Acid* melts at 121° (A. **292**, 134). *Diethylmalonic Nitrile* melts at 44° and boils at 92° (24 mm.).

Pentylmalonic Acid, $CH_3(CH_2)_4CH(CO_2H)_2$, melts at 82°. *Dipropylmalonic Acid*, $(CH_3 . CH_2 . CH_2)_2C(CO_2H)_2$, melts at 158°. *Cetylmalonic Acid*, $CH_3(CH_2)_{15}CH(CO_2H)_2$, melts at 121.5–122° (A. **204**, 130; **206**, 357; B. **24**, 2781).

THE ETHYLENE SUCCINIC ACID GROUP.

Ethylene succinic acid and its alkylic derivatives, as mentioned in the introduction, are characterized by the fact that when heated they break down into anhydrides and water. The anhydride formation takes place more readily in the alkylic succinic acids, the more hydrogen atoms of the ethylene residue of the succinic acid are replaced by alkyl radicals.

The alkylic succinic acids form anhydrides more readily with acetyl chloride, and are more volatile in aqueous vapor than their isomeric alkyl-n-glutaric acids (A. **285**, 212). The sym. dialkylic succinic acids show remarkable isomeric phenomena, which will be more fully explained under the symmetrical dimethylsuccinic acids (p. 444).

The following are characteristics of a succinic acid: (1) the anhydride; (2) the anilic acid, which appears in the chloroform, ethereal, or benzene solution of the anhydride; (3) the anil produced by heating the anilic acid, or by the action of phosphorus pentachloride or acetyl chloride upon it (A. **261**, 145; **285**, 226).

Ordinary Succinic Acid, or ethylene dicarboxylic acid, $CO_2H.CH_2.CH_2.CO_2H$, melting at 185°, is isomeric with methylmalonic acid, or isosuccinic acid (p. 441). It occurs in amber, in some varieties of lignite, in resins, in turpentine oils, and in animal fluids. It is formed in the oxidation of fats with nitric acid, in the fermentation of calcium malate or ammonium tartrate (A. **14**, 214), and in the alcoholic fermentation of sugar.

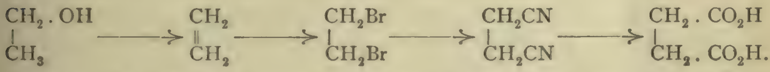
In the general methods of formation given on p. 430, ethylene succinic acid has been in part the chosen example. It is produced (1) by the oxidation of γ-butyrolactone.

(2) By the reduction of fumaric and maleïc acids with nascent hydrogen.

(3) By reducing (*a*) malic acid (oxysuccinic acid) and tartaric acid (dioxysuccinic acid) with hydriodic acid, or by the fermentation of these bodies; (*b*) by the action of sodium amalgam upon halogen succinic acids.

It is a nucleus-synthetic product obtained (4) by the action of finely divided silver upon brom-acetic acid. The yield is small.

(5*a*) By converting β-iodpropionic acid (p. 275) into cyanide and decomposing the latter with alkalies or acids. (5*b*) M. Simpson, in 1861, was the first to prepare it synthetically from ethylene, by converting the latter into cyanide. Succinic acid is formed on boiling its dinitrile with caustic potash or mineral acids:



$$\begin{array}{l}CH_2.OH\\ |\\ CH_3\end{array} \longrightarrow \begin{array}{l}CH_2\\ \|\\ CH_2\end{array} \longrightarrow \begin{array}{l}CH_2Br\\ |\\ CH_2Br\end{array} \longrightarrow \begin{array}{l}CH_2CN\\ |\\ CH_2CN\end{array} \longrightarrow \begin{array}{l}CH_2.CO_2H\\ |\\ CH_2.CO_2H.\end{array}$$

Ethidene chloride and potassium cyanide also yield ethylene cyanide (p. 441).

(6) The electrolysis of potassium ethyl malonic ester (p. 440) produces succinic ester.

(7) By the decomposition of aceto-succinic esters, (8) of ethanetricarboxylic acid, (9) of sym. ethane tetracarboxylic acid.

Succinic acid crystallizes in monoclinic prisms or plates, and has a faintly acid, disagreeable taste. It melts at 180° (185°) and distils at 235°, at the same sime decomposing partly into water and succinic anhydride. At the ordinary temperature it dissolves in 20 parts of water.

Uranium salts decompose aqueous succinic acid in sunlight into propionic acid and CO_2. The galvanic current decomposes its potassium salt into ethylene, carbon dioxide, and potassium (p. 90).

Paraconic Acids, γ-lactone carboxylic acids, are formed when sodium succinate is heated with aldehydes and acetic anhydride (Fittig, A. **255**, 1). When succinic acid, zinc chloride, sodium acetate, and acetic anhydride are heated to 200°, small quantities of aa'-dimethyl-β-acetyl pyrrol (B. **27**, R. 405) are produced. When calcium succinate is distilled, p-diketo-hexamethylene is produced in small quantities (B. **28**, 738).

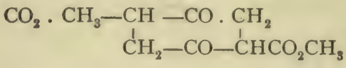
Salts, *succinates:* The *calcium salt*, $C_4H_4O_4Ca$, separates with 3 molecules of H_2O from a cold solution, but when it is deposited from a hot liquid it contains only

$1H_2O$. When ammonium succinate is added to a solution containing a ferric salt, all the iron is precipitated as reddish-brown basic ferric succinate (separation of iron from aluminium). When potassium ethyl succinate is electrolyzed, it yields *adipic ester* (p. 454).

Methyl Succinic Ester, $C_2H_4(CO_2 . CH_3)_2$, melts at 19°, and boils at 80°, under a pressure of 10 mm.

Ethyl Succinic Ester boils at 216°.

Sodium converts them into succino-succinic ester :



$$\begin{array}{l} CO_2 . CH_3\text{—}CH\text{—}CO . CH_2 \\ \qquad\qquad\quad | \qquad\qquad\; | \\ \qquad\qquad\; CH_2\text{—}CO\text{—}CHCO_2CH_3 \end{array}$$

Ethylene Succinic Ester, $C_2H_4<\begin{smallmatrix}CO_2\\CO_2\end{smallmatrix}>C_2H_4$, fuses at 90°.

Mono-alkylic Succinic Acids. Pyrotartaric Acid, Methyl Succinic Acid, $\begin{array}{l}CH_3 . CH . CO_2H \\ \; | \\ CH_2 . CO_2H\end{array}$, melts at 112°. It was first obtained in (1) the dry distillation of tartaric acid. It may be synthetically prepared (2) by heating pyroracemic acid, $CH_3 . CO . CO_2H$, alone to 170°, or with hydrochloric acid to 100° ; (3) by the action of nascent hydrogen upon the three isomeric acids: ita-, citra-, and mesa-conic acids: $C_5H_6O_4 + H_2 = C_5H_8O_4$; (4) from β-brombutyric acid and propylene bromide by means of the cyanide; (5) from α- and β-methyl aceto-succinic esters; and (6) from α- and β-methyl ethane tricarboxylic acid. The acid dissolves readily in water, alcohol, and ether. When quickly heated above 200° it decomposes into water and the anhydride. If, however, it be exposed for some time to a temperature of 200–210°, it splits into CO_2 and butyric acid. It suffers the same decomposition when in aqueous solution, if acted upon by sunlight in presence of uranium salts (B. **24**, R. 310).

Strychnine resolves it into its optically active components (B. **29**, 1254).

Potassium Salt, $C_5H_6O_4K_2$. The *calcium salt*, $C_5H_6O_4Ca + 2H_2O$, dissolves with difficulty in water. The *methyl ester* boils at 153° (20 mm.). The *ethyl ester* boils at 160° (22 mm.). The *dimethyl ester* boils at 197°. The *diethyl ester* boils at 218° (B. **26**, 337).

Ethyl Succinic Acid, $CO_2H . CH_2 . CH(C_2H_5)CO_2H$, melts at 98°. n-*Propyl Succinic Ester*, $CO_2H . CH_2 . CH(C_3H_7)CO_2H$, melts at 91° (A. **292**, 137).

Pimelic Acid, *Isopropyl Succinic Acid*, $(CH_3)_2 . CH . CH<\begin{smallmatrix}CH_2 . CO_2H\\CO_2H\end{smallmatrix}$, was first prepared by fusing camphoric acid and tanacetogen dicarboxylic acid (B. **25**, 3350) with caustic potash. It may be synthetically obtained from acetoacetic or malonic esters (A. **292**, 137), as well as from the products of the action of potassium cyanide upon isocaprolactone at 280° (C. 1897, I, 408). It melts at 114°.

Symm. Dialkylic Succinic Acids, $CO_2H . CHR' — CHR' . CO_2H$.

Symmetrical dimethyl succinic acid exists, like the other symmetrical disubstituted succinic acids,—*e. g.*, dibrom-succinic acid (p. 451), diethyl-, methyl-ethyl-, di-isopropyl-, and diphenyl-succinic acids,—in two different forms, having the same structural formulas.

Dioxysuccinic acid or tartaric acid occurs in two active and two inactive forms (one is decomposable and the other is not), which are satisfactorily explained by van t' Hoff's theory of *asymmetric* carbon atoms (p. 49). The pairs of isomeric dialkylic succinic acids, also containing asymmetric carbon atoms, manifest certain analogies with *para-* tartaric acid (racemic acid), and *anti-* or *meso*-tartaric acid. Hence it is assumed that their isomerism is due to the same cause. The higher melting, more difficultly soluble modification is called the *para*-form, while the *meso-* or *anti*-form is more readily soluble, and melts lower (Bischoff, B. **20**, 2990; **21**, 2106). However, this assumption is doubtful, inasmuch as not one of the constantly inactive dialkylic succinic acids has ever been converted into an active variety (B. **22**, 1819). Bischoff has set forth a theory of *dynamical isomerism* (B. **24**, 1074, 1085) in which he presents views in regard to the equilibrium positions of the atoms and radicals, joined to the two asymmetric carbon atoms, in the symmetrical dialkylic succinic acids.

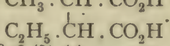
These (their esters) are produced as follows: By the saponification of dimethylethane tricarboxylic esters with hydrochloric acid; from dimethyl aceto-succinic ester by the elimination of the acetyl group; by heating α-halogen fatty-acids with reduced silver (B. **22**, 60), or more readily by the action of potassium cyanide upon α-monohalogen fatty-acids (B. **21**, 3160); by the reduction of dialkylic maleïc anhydrides, pyrocinchonic acid (p. 466), with sodium amalgam or hydriodic acid (B. **20**, 2737; **23**, 644). Both symmetrical dimethyl succinic acids are produced in all of these syntheses. They are separated by crystallization from water.

Sym. Dimethylsuccinic Acids, $CO_2H\,.\,CH(CH_3) — CH(CH_3)CO_2H$.

The *para*-acid is soluble in 96 parts of water at 14°. It forms needles and prisms, melting at 192°–194°. They sustain a partial loss of water upon melting. If the acid be heated for some time to 180°–200°, it yields a mixture of the anhydrides, $C_6H_8O_3$, of the *para-* and *anti*-acid (melting at 38° and 87°). With water each reverts to its corresponding acid. When acetyl chloride acts on the *para*-acid, its *anhydride* is the only product. It crystallizes from ether in rhombic plates, melts at 38°, and unites with water to form the pure para-acid (B. **20**, 2741; **21**, 3171; **22**, 389; **23**, 641; **29**, R. 420).

If the *para*-acid be heated to 130° with bromine, it yields pyrocinchonic anhydride, $C_6H_6O_3$ (p. 466). Both acids, when digested with bromine and phosphorus, yield the same brom-dimethyl succinic acid, $C_6H_9BrO_4$, melting at 91°. Zinc and hydrochloric acid change it to the *anti*-acid (B. **22**, 66). The *ethyl ester* of the para-acid (from the silver salt) boils at 219°; the *methyl ester* at 199°.

The *anti*-acid (analogous to anti-tartaric acid and maleïc acid) dissolves in 33 parts of water at 14°. It crystallizes in shining prisms, and fuses, after repeated crystallizations from water, at 120°–123°. It yields its *anhydride*, $C_6H_8O_3$, when heated to 200°. This melts at 87°. It regenerates the acid with water. If the anti-acid be heated with hydrochloric acid to 190°, it becomes the para-acid. The *methyl ester* boils at 200°; the *ethyl ester* at 222°. When the anti-acid is etherified with HCl, it yields a mixture of the esters of the anti- and para-acid (B. **22**, 389, 646; **23**, 639).

Sym. Methyl Ethyl Succinic Acids,  $\begin{array}{l} CH_3\,.\,CH\,.\,CO_2H \\ \quad\;\; | \\ C_2H_5\,.\,CH\,.\,CO_2H \end{array}$. The *para*-acid melts at 179°. The *anti-* or *meso*-acid melts at 84° (?) (A. **292**, 139).

Sym. Methyl Isopropyl Succinic Acids: The *para*-acid melts at 174°, and the *meso*-acid at 125° (B. **29**, R. 422).

Symmetrical Diethyl Succinic Acids.—The *para-acid* melts about 189–192°. It then loses water. The *anti-acid* melts at 129° (B. **20**, R. 416; **21**, 2085, 2105; **22**, 67; **23**, 650).

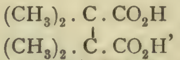
Sym. Dipropyl Succinic Acids: The *para*-acid melts at 197°; the *meso*-acid at 178° (B. **22**, 48).

Sym. Di-isopropyl Succinic Acid melts at 180° (A. **292**, 162).

Unsym. Dialkylic Succinic Acids.

Unsym. Dimethyl Succinic Acid, $CO_2H\,.\,CH_2\,.\,C(CH_3)_2\,.\,CO_2H$, melting at 140°, is synthetically prepared from α-dimethyl ethane-tricarboxylic ester—the product resulting from the action of bromisobutyric acid upon sodium malonic ester—on boiling it with sulphuric acid, and also from its nitrile (p. 449). Its imide (p. 448) resulted on oxidizing mesitylic acid (see this). *Unsym. Methyl-ethyl Succinic Acid* (A. **292**, 138, 153). *Unsym. Diethyl Succinic Acid*, $CO_2H . CH_2C(C_2H_5)_2COOH$, melts at 86°.

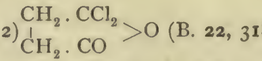
Trimethyl Succinic Acid, $CO_2H . CH(CH_3)—C(CH_3)_2 . CO_2H$, melting at 151° (A. **292**, 142), is produced on saponifying the tricarboxylic ester (B. **24**, 1923) produced in the action of bromisobutyric ester upon sodium methyl malonic ester, or sodium-*a*-cyanpropionic ester, as well as in the oxidation of camphoric acid (B. **26**, 2337), and by fusing camphoronic acid with potash (private communication from J. Bredt and Jagelki). The formation of trimethylsuccinic anhydride from camphoronic acid by distillation is rather important in the recognition of the constitution of camphor (B. **26**, 3047).

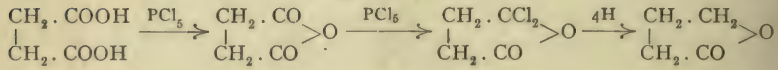
Tetramethyl Succinic Acid, 
$\begin{array}{l}(CH_3)_2 . C . CO_2H \\ \quad\quad\;\;\; | \\ (CH_3)_2 . C . CO_2H\end{array}$, is formed, together with trimethyl glutaric acid (p. 454), when *a*-bromisobutyric acid (or its ethyl ester) is heated with silver (B. **23**, 297; **26**, 1458); also by electrosynthesis from potassium dimethyl malonic ester, and fromazo butyronitrile (p. 361) (A. **292**, 220). It melts about 190–192°. It parts quite readily with water and passes into the **anhydride** (p. 447).

Chlorides of the Ethylene Succinic Acid Group.

Of the possible chlorides, the *monochloride*, $ClCOCH_2 . CH_2 . CO_2H$, is only known in the form of its *ethyl ester*, boiling at 144° (90 mm.), which results from the action of $POCl_3$ (B. **25**, 2748) upon sodium succinic ethyl ester.

Succinyl Chloride, melting at 0° and boiling at 190°, results from the action of PCl_5 upon succinic acid. Formerly it was given the formula (1) $COCl . CH_2 . CH_2 . COCl$ almost exclusively, although its behavior accorded better with formula

(2) 
$\begin{array}{l}CH_2 . CCl_2 \\ | \\ CH_2 . CO\end{array}\!\!>O$ (B. **22**, 3184):


$$\begin{array}{l}CH_2 . COOH \\ | \\ CH_2 . COOH\end{array} \xrightarrow{PCl_5} \begin{array}{l}CH_2 . CO \\ | \\ CH_2 . CO\end{array}\!\!>O \xrightarrow{PCl_5} \begin{array}{l}CH_2 . CCl_2 \\ | \\ CH_2 . CO\end{array}\!\!>O \xrightarrow{4H} \begin{array}{l}CH_2 . CH_2 \\ | \\ CH_2 . CO\end{array}\!\!>O$$

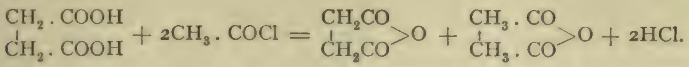
This latter view would make succinyl chloride a dichlor-substitution product of *butyrolactone*, into which it passes on reduction. The behavior of succinyl chloride toward zinc ethide is in harmony with its lactone formula, for it then yields *γ-diethylbutyrolactone* (p. 345), and in the presence of benzene and aluminium chloride it chiefly affords *γ-diphenylbutyrolactone* (B. **24**, R. 320). Ten per cent. of sym. *dibenzoyl ethane*, $C_6H_5CO . CH_2 . CH_2 . CO . C_6H_5$, is produced at the same time. Probably succinyl chloride is also a mixture of much γ-dichlorbutyrolactone and a little [butandiacid chloride], $ClCO . CH_2 . CH_2 . COCl$.

Pyrotartryl Chloride, $C_5H_6O_2Cl_2$, boils at 190–195° (B. **16**, 2624). *Unsym. Dimethylsuccinyl Chloride*, $C_6H_8O_2 . Cl_2$, boils at 200–202° (A. **242**, 138, 207).

Anhydrides of the Ethylene Succinic Acid Group.

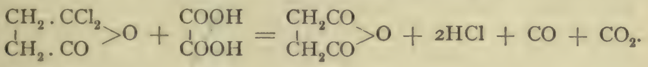
The easy anhydride formation is characteristic of ethylene succinic acid and its alkylic derivative. It proceeds the more readily the more the hydrogen atoms of the ethylene group are replaced by alcohol radicals (p. 442).

Formation.—(1) By heating the acids alone. (2) By the action of P_2O_5 (B. **28**, 1289), PCl_5 or $POCl_3$ (A. **242**, 150) upon the acids. (3) By treating the acids with the chloride or anhydride of a monobasic fatty acid, *e. g.*, acetyl chloride or acetic anhydride (Anschütz, A. **226**, 1):



$$\begin{array}{l}CH_2.COOH\\ |\\ CH_2.COOH\end{array} + 2CH_3.COCl = \begin{array}{l}CH_2CO\\ |\\ CH_2CO\end{array}{>}O + \begin{array}{l}CH_3.CO\\ |\\ CH_3.CO\end{array}{>}O + 2HCl.$$

(4) When the chloride of a dicarboxylic acid acts (*a*) upon the acid, or (*b*) upon anhydrous oxalic acid (A. **226**, 6):

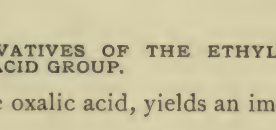


$$\begin{array}{l}CH_2.CCl_2\\ |\\ CH_2.CO\end{array}{>}O + \begin{array}{l}COOH\\ |\\ COOH\end{array} = \begin{array}{l}CH_2CO\\ |\\ CH_2CO\end{array}{>}O + 2HCl + CO + CO_2.$$

Succinic Anhydride, $\begin{array}{l}CH_2CO\\ |\\ CH_2CO\end{array}{>}O$, melts at 120° and boils at 261°. *Methyl Succinic Anhydride*, or *pyrotartaric anhydride*, melts at 31.5–32° and boils at 247°. *Ethyl Succinic Anhydride* boils at 243°. *Isopropyl Succinic Anhydride* boils at 250°. *Para-* and *Meso-s-dimethyl Succinic Anhydride* melt at 38° and 87°, respectively (B. **26**, 1460). *Meso-s-methyl-ethyl-* and *Meso-s-diethyl Succinic Anhydrides* melt at 244–245° and 245–246°. *Unsym. Dimethyl Succinic Anhydride* melts at 29° and boils at 219–220°. *Trimethyl Succinic Anhydride* melts at 31° and boils at 231° (760 mm.); 101° (12 mm.). *Tetramethyl Succinic Anhydride* melts at 147° and boils at 230.5°.

Properties and Behavior.—Succinic anhydride has a peculiar, faint, penetrating odor. It can be recrystallized from chloroform. It reverts to succinic acid in moist air. The conversion is more rapid if it is boiled with water. It yields succinic alkyl ester acids with alcohols. Ammonia and amines change it to succinamic and alkyl succinamic acids. PCl_5 changes it to succinyl chloride. Sodium amalgam reduces it to butyrolactone (B. **29**, 1193). If the anhydride is boiled for some time it loses CO_2 and changes to the dilactone of acetone diacetic acid, $CO(CH_2.CH_2.CO_2H)_2$ (see this). P_2S_3 converts succinic acid and sodium succinate into *thiophene*, $\overline{CH = CH - S - CH = CH}$ (see this). The reactions of very few of the homologues of succinic anhydride have thus far been accurately studied. They are similar to those of the latter.

Peroxides: *Succinyl Peroxide*,

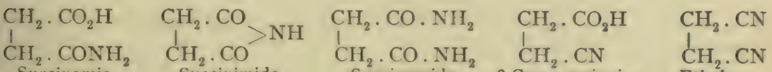


$$\begin{array}{l}CH_2.CO.O\\ |\qquad\quad\ |\\ CH_2.CO.O\end{array} \text{ or } \begin{array}{l}CH_2.C{<}^{O-O}\\ |\\ CH_2.CO\end{array}{>}O$$

is a white, crystalline body. It explodes below 100° if rapidly heated. It is formed by energetically shaking equimolecular quantities of succinyl chloride and sodium peroxide (B. **29**, 1724).

NITROGEN-CONTAINING DERIVATIVES OF THE ETHYLENE SUCCINIC ACID GROUP.

Ethylene succinic acid, like oxalic acid, yields an imide, a diamide, a nitrile acid and a dinitrile:



$$\begin{array}{l}CH_2.CO_2H\\ |\\ CH_2.CONH_2\end{array}\quad \begin{array}{l}CH_2.CO\\ |\\ CH_2.CO\end{array}{>}NH\quad \begin{array}{l}CH_2.CO.NH_2\\ |\\ CH_2.CO.NH_2\end{array}\quad \begin{array}{l}CH_2.CO_2H\\ |\\ CH_2.CN\end{array}\quad \begin{array}{l}CH_2.CN\\ |\\ CH_2.CN\end{array}$$

Succinamic Acid — Succinimide — Succinamide — β-Cyanpropionic Acid — Ethylene Cyanide.

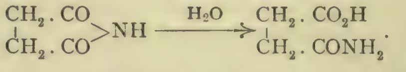
(*a*) **Amic Acids.**—Most of these have been prepared by decomposing the imides with alkalies or baryta water. They are also formed on adding ammonia, primary aliphatic amines (and aromatic amines, *e.g.*, aniline and phenylhydrazine) to acid anhydrides. They behave like oxamic acid (p. 435). When heated, or when treated with dehydrating agents, *e.g.*, PCl_5 or $CH_3 . COCl$, they become imides, which bear the same relation to them that the anhydrides sustain to the dicarboxylic acids. *Succinamic Acid*, $CO_2H . CH_2 . CH_2 . CONH_2$, is obtained from succinimide by the action of baryta water. *Succinethylamic Acid*, $CO_2H . CH_2 . CH_2 . CONHC_2H_5$ (A. 251, 319). *Succinalic Acid*, $CO_2H . CH_2 . CH_2 . CONHC_6H_5$ (B. **20**, 3214). *Unsym. Dimethyl Succinalic Acid* melts at 189°.

(*b*) **Imides.**—These are produced (1) on heating the acid anhydrides in a current of ammonia; (2) when the ammonium salts, diamides and amic acids are heated. They show a symmetrical structure, as will be explained in connection with succinanil.

Succinimide, $\begin{matrix}CH_2 . CO\\ | \\ CH_2 . CO\end{matrix}\!\!>NH$, melting at 126° and boiling at 288°, crystallizes with water, and manifests the character of an acid, as the hydrogen of the NH-group can be replaced by metals.

Potassium Succinimide, $C_2H_4(CO)_2NK$; *Sodium Succinimide* (B. **28**, 2353); *Silver Succinimide* (A. **215**, 200); *Potassium Tetrasuccinimide-tri-iodo-iodide*, $(C_4H_5O_2N)_4I_3 . KI$ (B. **27**, R. 478; **29**, R. 298).

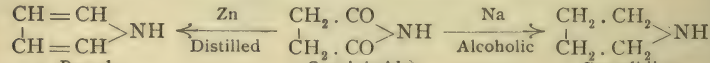
The cyclic imides are readily broken down by alkalies and alkaline earths:



$$\begin{matrix}CH_2 . CO\\ | \\ CH_2 . CO\end{matrix}\!\!>NH \xrightarrow{H_2O} \begin{matrix}CH_2 . CO_2H\\ | \\ CH_2 . CONH_2\end{matrix}.$$

On distilling succinimide with zinc dust, oxygen is withdrawn and pyrrol (see this) is formed.

Pyrrolidine, C_4H_9N (B. **20**, 2215), is formed in the action of sodium upon succinimide dissolved in absolute alcohol:



$$\underset{\text{Pyrrol}}{\begin{matrix}CH = CH\\ | \\ CH = CH\end{matrix}\!\!>NH} \xleftarrow[\text{Distilled}]{\text{Zn}} \underset{\text{Succinimide}}{\begin{matrix}CH_2 . CO\\ | \\ CH_2 . CO\end{matrix}\!\!>NH} \xrightarrow[\text{Alcoholic}]{\text{Na}} \underset{\text{Pyrrolidine.}}{\begin{matrix}CH_2 . CH_2\\ | \\ CH_2 . CH_2\end{matrix}\!\!>NH}$$

Pyrrol Succinimide Pyrrolidine.

Hypochlorous acid, and hypobromous acid acting on succinimide, and iodine upon silver succinimide produce: *Succinchlorimide*, $C_2H_4(CO)_2NCl$, melting at 148°; *succinbromimide*, $C_2H_4(CO)_2 NBr$, melting at 173–175° with decomposition, and *succiniodo-imide* (B. **26**, 985). Phosphorus pentachloride converts succinimide into *dichlormaleïn-imide chloride*, $\begin{matrix}CCl . CO\\ \| \\ CCl . CCl_2\end{matrix}\!\!>NH$; pentachlorpyrrol, C_4Cl_5N, and the heptachloride, C_4Cl_7O (A. **295**, 86). Bromine and caustic potash convert succinimide into β-amido-propionic acid (p. 358). Sodium methylate changes succinbromimide by a molecular rearrangement into *carbmethoxy-β-amidopropionic ester*, $CH_3O . CO . NH . CH_2 . CH_2 . CO_2 . CH_3$, melting at 33.5° (B. **26**, R. 935).

Methyl Succinimide, $C_2H_4{<}{\begin{matrix}CO\\CO\end{matrix}}{>}N . CH_3$, melts at 66.5° and boils at 234°. It is obtained from the oxime of lævulinic acid (p. 379) by the action of concentrated sulphuric acid (A. **251**, 318).

Ethyl Succinimide, $C_2H_4{<}{\begin{matrix}CO\\CO\end{matrix}}{>}N . C_2H_5$, melts at 26° and boils at 234°. It is formed when ethyl iodide acts upon potassium succinimide. It yields ethyl pyrrol when it is distilled with zinc dust. *Isopropyl Succinimide* melts at 61° and boils at 230°. *Isobutyl Succinimide* melts at 28° and boils at 247° (B. **28**, R. 600).

Phenyl Succinimide, Succinanil, $C_2H_4(CO)_2 . N . C_6H_5$, melting at 150°, is converted by PCl_5 into dichlormaleïc-anil-dichloride, $\begin{array}{l}CCl - CO \\ \| \\ CCl - CCl_2\end{array}\!>NC_6H_5$, the lactam of γ-anilido-perchlorcrotonic acid and tetrachlorphenyl pyrrol, $\begin{array}{l}CCl = CCl \\ | \\ CCl = CCl\end{array}\!>NC_6H_5$. This last fact, and the reduction of dichlormaleïc dichloride to γ-anilido-butyrolactam or n-phenyl butyrolactam, $\begin{array}{l}CH_2 . CO \\ | \\ CH_2 . CH_2\end{array}\!>NC_6H_5$, indicate that the symmetrical formula properly falls to both succinanil and succinimide (A. **295**, 39, 88).

Unsym. Dimethyl Succinanil melts at 85°. *Trimethyl Succinanil* melts at 129°. *Tetramethyl Succinanil* melts at 88° (A. **285**, 234; **292**, 184, 176).

v-Anilido-succinimide, $C_2H_4(CO)_2N - NHC_6H_5$, melts at 155° (J. pr. Ch. [2], **35**, 293).

Pyrotartrimide, $\begin{array}{l}CH_3 . CH . CO \\ \quad\;\; | \\ \quad\;\; CH_2 . CO\end{array}\!>NH$, melts at 66°. s-*Dimethyl Succinimide* (B. **22**, 646). *Unsym. Dimethyl Succinimide*, melting at 106°, is produced by oxidizing mesitylic acid (see this) (A. **242**, 208; B. **14**, 1075). *Pimelimide* melts at 60° (A. **220**, 276).

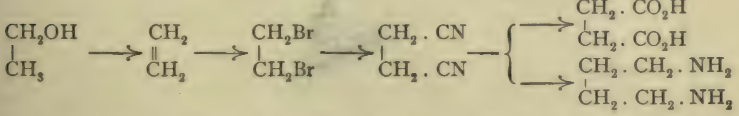
(*c*) Diamides and Hydrazides.

Succinamide, $C_2H_4\!<\!\begin{array}{l}CO . NH_2 \\ CO . NH_2\end{array}$, is produced like oxamide. It crystallizes from hot water in needles. At 200° it decomposes into ammonia and succinimide.

Succindibrom-diamide, $NH_2CO[CH_2]_2CONBr_2$, is obtained from succinamide and BrOK (see also β-lactyl urea, p. 402). *Pyrotartramide* melts at 225° (B. **29**, R. 509). *Succinhydrazide*, $\begin{array}{l}CH_2 . CONH . NH_2 \\ | \\ CH_2 . CONH . NH_2\end{array}$, melts at 167° (J. pr. Ch. [2], **51**, 190).

(*d*) **Cyclic Diamides.**—*Succinyl Ethylene Diamide*, $\begin{array}{l}CH_2 . CONH . CH_2 \\ | \qquad\qquad\quad\;\; | \\ CH_2 . CONH . CH_2\end{array}$ (B. **27**, R. 589). *Succinphenylhydrazide*, 1-Phenyl-3.6-orthopiperazone, $\begin{array}{l}CH_2 . CO . N . C_6H_5 \\ | \qquad\quad\; | \\ CH_2 . CO . NH\end{array}$, melting at 199°, is obtained from the hydrochloride of phenylhydrazine and succinyl chloride (B. **26**, 674, 2181).

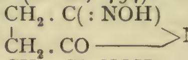
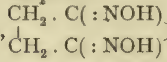
(*e*) **Nitriles.**—*Nitrile acids* have not been studied to any great extent. Certain *dinitriles* have been prepared by the action of potassium cyanide upon alkylen bromides, the addition-products, formed by the union of bromine with the olefines. By absorbing water these dinitriles become the ammonium salts of the corresponding acids, the synthesis of which they thus facilitate. When reduced, they take up eight atoms of hydrogen and become the diamines of the glycols—*e. g.*:



$$\begin{array}{l}CH_2OH \\ | \\ CH_3\end{array} \longrightarrow \begin{array}{l}CH_2 \\ \| \\ CH_2\end{array} \longrightarrow \begin{array}{l}CH_2Br \\ | \\ CH_2Br\end{array} \longrightarrow \begin{array}{l}CH_2 . CN \\ | \\ CH_2 . CN\end{array} - \left\{\begin{array}{l} \longrightarrow \begin{array}{l}CH_2 . CO_2H \\ | \\ CH_2 . CO_2H\end{array} \\ \longrightarrow \begin{array}{l}CH_2 . CH_2 . NH_2 \\ | \\ CH_2 . CH_2 . NH_2\end{array}\end{array}\right.$$

Succino-nitrile, *Ethylene Cyanide*, $CN . CH_2 . CH_2 . CN$, melting at 54.5°, and boiling at 158–160° (20 mm.), is amorphous, transparent, readily soluble in water, chloroform and alcohol, but sparingly soluble in ether. It is also obtained by the electrolysis of potassium cyanacetate (p. 76).

It yields ethylene succinic acid when saponified, and tetramethylene diamine upon reduction. It combines with 4HI (B. **25**, 2543). Paraformaldehyde, glacial acetic acid and sulphuric acid convert it into *methylene succinimide*, $(C_2H_4 . C_2O_2N)_2CH_2$, melting above 270° (J. pr. Ch. [2], **50**, 3).

(*f*) **Oximes.**—*Succinylhydroxamic Acid*, $CO_2H . CH_2 . CH_2 . C(:N . OH)OH$ (B. **28**, R. 999). *Succinylhydroxamic Tetracetate*, $AcO(AcON:)C . CH_2 . CH_2 . C(:N . OAc)OAc$, melts at 130° (B. **28**, 754). Hydroxylamine converts succinonitrile into *succinimidoxime*,  $\left.\begin{array}{l}CH_2 . C(:NOH) \\ | \\ CH_2 . CO\end{array}\right>NH$, melting at 197° (B. **24**, 3427) and *succinimide dioxime*,  $\left.\begin{array}{l}CH_2 . C(:NOH) \\ | \\ CH_2 . C(:NOH)\end{array}\right>NH$, melting at 207° (B. **22**, 2964).

Pyrotartaronitrile melts at 12° (A. **182**, 327; B. **28**, 2952).

Unsym. Dimethylsuccinonitrile, $CN . CH_2 . C(CH_3)_2 . CN$, boils at 218–220° (B. **22**, 1740).

HALOGEN SUBSTITUTION PRODUCTS OF THE SUCCINIC ACID GROUP.

The *monosubstitution* products are obtained (1) by the direct action of halogens upon the acids, their esters, chlorides or anhydrides. In case of the acids, it is advisable to act upon them with amorphous phosphorus and bromine (B. **21**, R. 5); (2) by the addition of an halogen hydride to the corresponding unsaturated dicarboxylic acid of the *fumaric* and *maleïc* group (A. **254**, 161); (3) by the action of an halogen hydride and (4) of PCl_5 or PBr_5 upon the corresponding α-monoxyethylene dicarboxylic acids (A. **130**, 21); (5) from amido-succinic acids by means of potassium bromide, sulphuric acid, bromine and nitric oxide (B. **28**, 2769).

Inactive *chlorsuccinic acid*, $CO_2H . CHCl . CH_2 . CO_2H$, from fumaric acid and hydrochloric acid, melts at 151.5° to 152°. The *dimethyl ester* boils at 106.5° (14 mm.). The *diethyl ester* boils at 122° (15 mm.). The *anhydride* melts at 40–41° and boils at 125–126° (12 mm.) (A. **254**, 156; B. **23**, 3757).

d-*Chlorsuccinic Acid* melts with decomposition at 176°. It is obtained from l-malic acid by means of PCl_5 and water. Its silver salt becomes d-malic acid when it is boiled with water. The *dimethyl ester* boils at 107° (15 mm.); the *chloride* at 92° (11 mm.); the *anhydride* at 138° (20 mm.) (B. **28**, 1289).

l-*Chlorsuccinic Acid* is prepared from l-aspartic acid, which can be changed to l-malic acid. Starting, therefore, with l-aspartic acid, it is not only possible to prepare l-chlorsuccinic acid and l-malic acid, but with the aid of the latter we can obtain d-chlorsuccinic acid, which can be transposed into δ-malic acid (p. 68):

$$\begin{tikzcd}
 & \text{l-Chlorsuccinic Acid} \arrow[d] & \text{d-Malic Acid} \arrow[l] \\
\text{l-Aspartic Acid} \arrow[ur] \arrow[r] & \text{l-Malic Acid} \arrow[r] & \text{d-Chlorsuccinic Acid.} \arrow[u]
\end{tikzcd}$$

Inactive *bromsuccinic acid*, $CO_2H . CHBr . CH_2 . CO_2H$, from hydrobromic acid and fumaric acid, melts at 160°. Its *dimethyl ester* boils at 110° (10 mm.). Its *anhydride* melts at 30–31° and boils at 137° (11 mm.).

d-*Bromsuccinic Dimethyl Ester*, from l-malic acid and PBr_5, boils at 124° (20 mm.) (B. **28**, 1291).

l-*Bromsuccinic Acid*, from l-aspartic acid (B. **28**, 2770; **29**, 1699), melts with decomposition at 173°.

The free, inactive acids and their esters, when heated at the ordinary pressure, break down into an halogen hydride and fumaric acid and its ester, while the anhydrides yield the halogen hydride and maleïc anhydride (A. **254**, 157). Moist silver oxide converts bromsuccinic acid into *inactive malic acid* (see this), which can thus be synthesized in this way.

The addition of an haloid acid to ita-, citra-, and mesaconic acids produces *chlorpyrotartaric acids*, $C_5H_7ClO_4$:

(1) *Itachlorpyrotartaric Acid*, melting at 140–141° (compare paraconic acid, see this, and itamalic acid).

(2) *Mesa-* or *Chlorpyrotartaric Acid*, melting at 129° (A. **188**, 51).

Brompyrotartaric Acids, $C_5H_2BrO_4$:

(1) *Itabrompyrotartaric Acid*, melting at 137°.

(2) *Citrabrompyrotartaric Acid*, melting at 148°.

Dihalogen Substitution Products are produced (1) by the direct action of bromine and water upon the acids; (2) by the addition of halogen hydride to the monohalogen unsaturated acids of the *fumaric* and *maleïc* series; (3) by the addition of halogens—particularly bromine—to the unsaturated acids of the fumaric and maleïc series.

When hydrobromic acid is added to fumaric and maleïc acids they yield the same monobromsuccinic acid, but with bromine, fumaric acid forms the sparingly soluble *dibromsuccinic acid*, while maleïc acid and bromine yield the easily soluble *isodibromsuccinic acid* and fumaric acid. These two dibromsuccinic acids have the same structural formula, they are symmetrically constructed, and their isomerism is probably due to the same cause prevailing with the s-dialkylic succinic acids (p. 444). Yet they are intimately related to racemic and mesotartaric acids, which were first synthetically prepared by means of the dibromsuccinic acids. Inasmuch as fumaric acid yields racemic acid when oxidized, therefore the sparingly soluble dibromsuccinic acid, the dibrom addition product of fumaric acid, should correspond to racemic acid, and isodibromsuccinic acid to meso-tartaric acid. However, the transposition reactions of the dibromsuccinic acids show many contradictions.

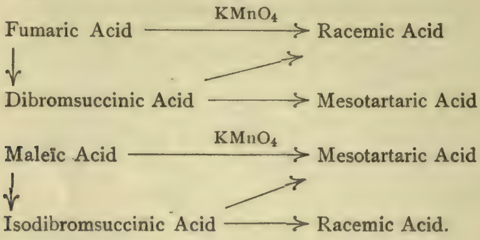
Dichlorsuccinic Acid, from fumaric acid and liquid chlorine, melts at 215° with decomposition. The *methyl ester* melts at 32° (A. **280**, 210).

Isodichlorsuccinic Acid melts with decomposition at 170°. It is obtained from the *anhydride*, melting at 95°, the addition product of maleïc anhydride and liquid chlorine. When heated, the anhydride changes to chlormaleïc anhydride (A. **280**, 216).

Dibrom-succinic Acid, $C_2H_2Br_2(CO_2H)_2$, consists of prisms which are not very soluble in cold water. When heated to 200–235° it breaks up into HBr and brom-maleïc acid, and with acetic anhydride it yields brom-maleïc anhydride and acetyl bromide. The *methyl ester* melts at 62°; the *ethyl ester* at 68°.

Isodibrom-succinic Acid, $C_2H_2Br_2(CO_2H)_2$, is very soluble in water. It melts at 160° and decomposes at 180° into HBr and brom-fumaric acid (p. 464). Its *anhydride*, $C_2H_2Br_2(CO)_2O$, from maleïc anhydride and bromine, melts at 42°. At 100° it breaks down into HBr and brom-maleïc anhydride (A. **280**, 207). The *anilic acid* melts at 144°. The *anil* melts at 177° (A. **292**, 233; **239**, 143). When reduced, both acids yield ethylene succinic acid; when boiled with potassium iodide they change to fumaric acid, while boiling sodium hydroxide or baryta water converts them into *acetylene dicarboxylic acid* (A. **272**, 127). The sparingly soluble dibrom-acid, when boiled with water, passes into brom-maleïc acid, while the readily soluble acid, under like treatment, becomes brom-fumaric acid. Two hundred parts of boiling water convert the difficultly soluble dibrom-acid, in the presence of the brominated unsaturated acid, into mesotartaric acid, together with a little racemic acid, while the readily soluble acid yields much racemic acid and but little of the mesotartaric acid (A. **292**, 295).

The silver salt of the difficultly soluble dibrom-acid changes on boiling with water to mesotartaric acid (see this), while racemic acid is obtained under similar conditions from the easily soluble isodibromsuccinic acid (B. **21**, 268). Much *mesotartaric acid* with but little *racemic acid* is formed on boiling the barium or calcium salt of the difficultly soluble dibrom-succinic acid. The contradictions in these reactions are made clearer in the scheme which follows:



Trichlorsuccinic Acid is a crystalline, exceedingly soluble mass, obtained on exposing chlormaleïc acid, water and liquid chlorine to sunlight (A. 280, 230).

Tetrachlorsuccinanil, melting at 157°, is formed together with dichlormaleïnanil chloride (p. 464), when PCl_5 acts upon dichlormaleïnanil (A. 295, 33).

Tribrom-succinic Acid, $C_2HBr_3(CO_2H)_2$, is produced when bromine (and water) acts upon brom-maleïc acid and isobrom-maleïc acid; it consists of acicular crystals, which melt at 136-137°. The aqueous solution decomposes at 60° into CO_2, HBr, and dibromacrylic acid, $C_3H_2Br_2O_2$, which melts at 85°.

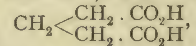
Dibrompyrotartaric Acids.—The addition of bromine to ita-, citra- and mesaconic acids gives rise to three dibrompyrotartaric acids, which upon reduction revert to the same pyrotartaric acid (p. 444).

The **ita-, citra-** and **mesa-dibrompyrotartaric acids**, $C_5H_6Br_2O_4$, are distinguished by their different solubility in water. The ita- compound changes to aconic acid, $C_5H_4O_4$, when the solution of its sodium salt is boiled; the citra- and mesa-compounds, on the other hand, yield brom-methacrylic acid (p. 283).

An excess of caustic potash will convert citradibrompyrotartaric acid into brommesaconic acid (p. 464).

GLUTARIC ACID GROUP.

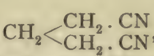
Glutaric acid and its alkylic derivatives, like ethylene succinic acid, are characterized by the fact that when they are heated they break down into anhydride and water. The anhydrides readily yield anilic acids, from which anils can be obtained by the withdrawal of water. The glutaric acids resemble the ethylene succinic acids in deportment, but they are changed to anhydrides with greater difficulty by acetyl chloride, and are not so volatile with steam.



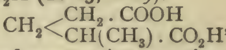
Glutaric Acid, $CH_2<\begin{matrix}CH_2 . CO_2H\\CH_2 . CO_2H\end{matrix}$, *Normal Pyrotartaric Acid* [*Pentan diacid*], is isomeric with monomethyl succinic acid or ordinary pyrotartaric acid, as well as with ethyl and dimethylmalonic acids (p. 437). It was first obtained by the reduction of α-oxyglutaric acid with hydriodic acid. It may be synthetically prepared from trimethylene bromide (p. 303), through the cyanide; from acetoacetic ester by means of the aceto-glutaric ester (see this); from glutaconic acid (p. 467), and from propane tetracarboxylic acid or methylene dimalonic acid, $C_3H_4(CO_2H)_4$, by the removal of $2CO_2$. Glutaric acid crystallizes in large monoclinic plates, melts at 97°, and distils near 303°, with scarcely any decomposition. It is soluble in 1.2 parts water at 14°.

The *calcium salt*, $C_5H_6O_4Ca + 4H_2O$, and *barium salt*, $C_5H_6O_4Ba + 5H_2O$ (like calcium butyrate, p. 247), are easily soluble in water; the first more readily in cold than in warm water. The *monomethyl ester* boils at 153° (20 mm.) (B. **26**, R. 276). The *ethyl ester* boils at 237°. The *anhydride*, $C_5H_6O_3$, forms on slowly heating the acid to 230–280°, and in the action of acetyl chloride on the silver salt of the acid. It crystallizes in needles, melting at 56–57°.

Glutarimide, $C_3H_6(CO)_2NH$, results by the distillation of ammonium glutarate and by the oxidation of pentamethylene imide (p. 315), or piperidine with H_2O_2 (B. **24**, 2777). It yields a little pyridine when it is heated with zinc dust (B. **16**, 1683). It melts at 152°.

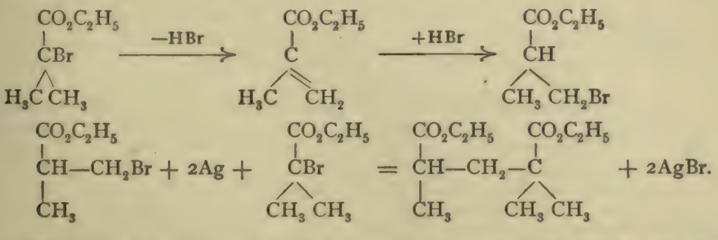
Nitrile of Glutaric Acid, Trimethylene Cyanide,  $CH_2{<}\begin{matrix}CH_2.CN\\CH_2.CN\end{matrix}$, boiling at 286°, is obtained from trimethylene bromide and potassium cyanide. Alcohol and sodium convert it into pentamethylene diamine (p. 313) and piperidine (p. 315), while it yields glutarimide-dioxime with hydroxylamine (B. **24**, 3431).

Pentachlorglutaric Acid, $CO_2H.CCl_2.CHCl.CCl_2.CO_2H$ (B. **25**, 2219).

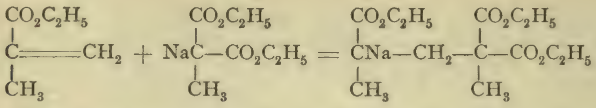
Monoalkylic Glutaric Acids.—a-Methyl Glutaric Acid,  $CH_2{<}\begin{matrix}CH_2.COOH\\CH(CH_3).CO_2H\end{matrix}$, melting at 76°, results from the reduction of saccharone, and on treating camphorphorone with $KMnO_4$ (B. **25**, 265). It may by synthesized by starting with methylacetoacetic ester and β-iodopropionic acid, and when KCN acts upon lævulinic acid. It is a by-product in the decomposition of isobutylene tricarboxylic ester.

P_2S_3 converts it into *methylpentiophene*. The *anhydride* melts at 40° and boils at 283°. See A. **292**, 211, for the *anilic acids*. *a-Ethyl Glutaric Acid* melts at 60° and boils at 195° (30 mm.). The *anhydride* boils at 275°. *Anilic Acids*, A. **292**, 144, 215. *β-Methyl Glutaric Acid*, ethidene diacetic acid, $CH_3.CH(CH_2.CO_2H)_2$, melting at 86°, is formed from crotonic ester and sodium malonic ester. The *anhydride* melts at 46° and boils at 283° (B. **24**, 2888). *β-Ethyl Glutaric Acid*, propidene diacetic acid, melts at 67°. The two acids are obtained from ethidene and propidenedimalonic acid.

Di- and Tri-alkylic Glutaric Acids are produced together with tri- and tetramethyl succinic acids in the syntheses of these latter acids from a-bromisobutyric acid with silver, with methyl malonic ester, etc. In order to explain the formation of these unexpected alkylic glutaric acids in these reactions, it has been assumed that a portion of the a-bromisobutyric acid gives up HBr and passes into methacrylic ester. In the silver reaction the BrH attaches itself to the methyl acrylic esters, and the silver withdraws bromine from the a- and β-bromisobutyric ester, whereby the residues unite to trimethyl glutaric ester (B. **22**, 48, 60):



In the second stage sodium methyl malonic ester attaches itself to methyl acrylic ester, and when the addition product is saponified it yields dimethyl glutaric acid (B. **24**, 1041, 1923):



$$\underset{\displaystyle CH_3}{\overset{\displaystyle CO_2C_2H_5}{C}}{=\!=}CH_2 + Na\underset{\displaystyle CH_3}{\overset{\displaystyle CO_2C_2H_5}{C}}-CO_2C_2H_5 = \underset{\displaystyle CH_3}{\overset{\displaystyle CO_2C_2H_5}{C}}Na-CH_2-\underset{\displaystyle CH_3}{\overset{\displaystyle CO_2C_2H_5}{C}}-CO_2C_2H_5$$

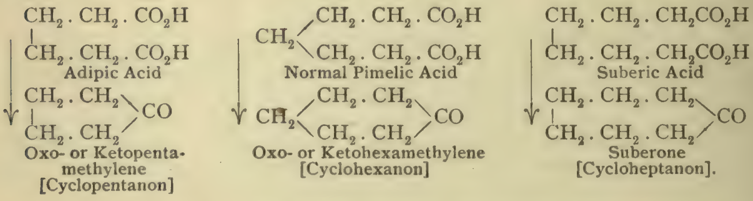
αα₁-Dimethyl Glutaric Acids, $CH_2[CH(CH_3)CO_2H]_2$, melting at 127° and 140° (A. **292**, 146; B. **29**, R. 421), also result from the action of methylene iodide upon sodium α-cyanpropionic ester. Bromine converts both acids into α-brom-products, from which oxydimethyl glutaric acids and their lactones are obtained (B. **25**, 3221; A. **292**, 146). *αα₁-Diethyl Glutaric Acids* (A. **292**, 204). *αβ-Dimethyl Glutaric Acid* (A. **292**, 147; B. **29**, 2058).

Unsym. αα₁-Dimethyl Glutaric Acid, $CO_2H \,.\, C(CH_3)_2 \,.\, CH_2 \,.\, CH_2 \,.\, CO_2H$, melts at 85°, and its anhydride at 38°. *ββ-Dimethyl Glutaric Acid*, $CO_2H \,.\, CH_2C(CH_3)_2$-$CH_2CO_2H$, from dimethyl acrylic ester with sodium or potassium malonic ester, and subsequent decomposition of the dimethyl propane tricarboxylic acid (A. **292**, 145; C. 1897, I, 28), melts at 100°, and its anhydride at 124°. The *anilic acid* melts at 134°.

α, α, α₁-Trimethyl Glutaric Acid, $CO_2H \,.\, CH(CH_3)CH_2C(CH_3)_2 \,.\, CO_2H$, melts at 97° (compare tetramethyl succinic acid). Its *anhydride* melts at 96° and boils at 262° (A. **292**, 220).

GROUP OF ADIPIC ACID AND HIGHER NORMAL PARAFFIN DICARBOXYLIC ACIDS.

Adipic acid and its alkylic derivatives volatilize under reduced pressure without decomposition. They, together with normal pimelic acid and suberic acid, are characterized by the fact that when their calcium salts are heated *cyclic ketones* result (J. Wislicenus, A. **275**, 309):

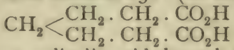


When adipic acid and the higher saturated dicarboxylic acids are boiled with acetyl chloride, anhydrides are also produced. It is not known whether they should receive the simple molecular formula or a multiple of it (B. **27**, R. 405; C. 1896, II, 1091).

Adipic Acid [Hexan diacid], $CO_2H[CH_2]_4CO_2H$, was first obtained by oxidizing fats with nitric acid. It is also produced (1) in the reduction of *hydromuconic acid* (p. 467). It is synthetically prepared (2) by heating β-iodpropionic acid, with reduced silver, to 130–140°, or with copper to 160° (B. **28**, R. 466); (3) by the electrolysis of potassium ethyl succinic ester (A. **261**, 117), and (4) from ethylene dimalonic acid or butane tetracarboxylic acid. Sodium converts adipic ester into β-ketopentamethylene monocarboxylic ester (B. **27**, 103). Cyclopentanon is produced when the calcium salt is distilled.

a-Methyl Adipic Acid melts at 64°. *a-Ethyl Adipic Acid* is a liquid. *β-Methyl Adipic Acid* melts at 89° and boils at 210–212° (14.5 mm.). It results from the oxidation of pulegone and menthone (A. **292,** 148).

aa_1-Diethyl Adipic Acids have been prepared from the corresponding aa_1-dialkylic ethylene dimalonic acids. *aa_1-Dimethyl Adipic Acid* (see B. **27,** 1578). *aa_1-Diethyl Adipic Acids* (see B. **28,** R. 300). *a-Bromadipic Acid* melts at 131° (B. **28,** R. 466).

Normal Pimelic Acid [Heptan diacid],  $CH_2<\begin{matrix}CH_2.CH_2.CO_2H\\CH_2.CH_2.CO_2H\end{matrix}$ (A. **292,** 150), first prepared by oxidizing suberone, and from salicylic acid through the action of sodium in amyl alcohol solution (A. **286,** 259); by heating furonic acid, $C_7H_8O_5$, with HI, and in the oxidation of fats with nitric acid, can be obtained synthetically from trimethylene bromide and malonic ester by heating pentamethylene tetracarboxylic acid, which is the first product of the reaction (B. **26,** 709). It melts at 105°. When its lime salt is distilled [cyclohexanon] is produced (p. 454).

Alkylic Pimelic Acids: a-, β-, and γ-Methyl Pimelic Acids melt at 54°, 49°, and 56°. They are formed when the o-, m-, and p-cresotic acids, or better their dibrom-derivatives, are reduced by amyl alcohol and sodium (A. **295,** 173). The a-acid may also be prepared from the corresponding tetracarboxylic acid (B. **29,** 729).

aa_1-Dimethyl Pimelic Acids melt at 81° and 76° (B. **28,** R. 465).

aβa-Trimethyl Pimelic Acid boils at 214° (15 mm.) (B. **28,** 2943).

aa_1-Dibrompimelic Acid melts at 141°. Its *diethyl ester*, boiling at 224° (28 mm.), when acted upon by sodium ethylate becomes Δ′-cyclopentene-dicarboxylic acid.

Suberic Acid [Octan diacid], $C_8H_{14}O_4$, is obtained by boiling corks (B. **26,** 3089), or fatty oils, with nitric acid (B. **26,** R. 814). It melts at 140°. Its *ethyl ester* boils at 280–282°. It has been synthesized by electrolyzing potassium ethyl glutarate. *Suberone* (p. 454) results when its calcium salt is distilled (A. **275,** 356). Its *anhydride* melts at 62°. The *dihydrazide* melts at 185°. The *diazide* melts at 25° (B. **29,** 1166). See also 1.6-hexamethylene diamine, p. 313.

Higher dibasic acids are produced by oxidizing the fatty acids or oleic acids with nitric acid. They always form succinic and oxalic acids at the same time. The higher acetylene carboxylic acids usually decompose into the acids $C_nH_{2n}O_4$, when oxidized with fuming nitric acid. The mixture of acids that results is separated by fractional crystallization from ether; the higher members, being less soluble, separate out first (B. **14,** 560). Such acids have also been produced by the breaking-down of ketoximic acids through the action of concentrated sulphuric acid, *e. g.*, sebacic acid from ketoxime stearic acid. See p. 285 for the importance of this reaction.

Lepargylic Acid, $C_9H_{16}O_4$, **Azelaic Acid** [Nonan diacid], is best prepared by oxidizing castor oil (B. **17,** 2214). It melts at 106°. It can be synthesized from pentamethylene bromide and sodium acetoacetic ester (B. **26,** 2249). Its *anhydride* melts at 52°.

Sebacic Acid, $C_{10}H_{18}O_4$ [Decan diacid], is obtained by the dry distillation of oleic acid, by the oxidation of stearic acid and spermaceti, from ketoxime stearic acid, and from heptane tetracarboxylic acid (B. **27,** R. 413). The acid melts at 133°. The *anhydride* melts at 78°.

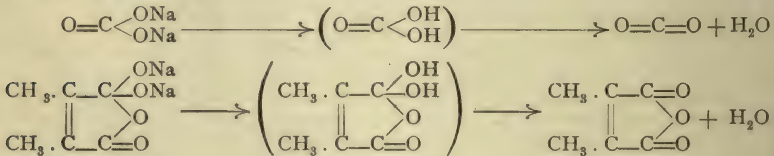
Brassylic Acid, $C_{11}H_{20}O_4$, obtained by oxidizing behenoleic and erucic acids, melts at 114° (B. **26,** 639, R. 795, 811).

Roccellic Acid, $C_{17}H_{32}O_4$, occurs free in *Rocella tinctoria*. It melts at 132°.

B. OLEFINE DICARBOXYLIC ACIDS, $C_nH_{2n-4}O_4$.

The acids of this series bear the same relation to those of the oxalic acid series that the acids of the acrylic series bear to the fatty acids.

The free acid hydrates of all the acids of the oxalic series are known, but in the case of the unsaturated acids there are some, like carbonic acid, which only exist in the anhydride condition. When the attempt is made to liberate the acids from their salts, they immediately split off water and pass into the corresponding anhydrides, *e. g.*, dimethyl and diethyl-maleïc anhydrides. The analogy of such acids with carbonic acid, to which reference has already been made (p. 290), manifests itself in the following constitutional formulas (A. **254**, 169; **259**, 137):



$$O{=}C{<}\genfrac{}{}{0pt}{}{ONa}{ONa} \longrightarrow \left(O{=}C{<}\genfrac{}{}{0pt}{}{OH}{OH}\right) \longrightarrow O{=}C{=}O + H_2O$$

Pyrocinchonate or Dimethyl maleäte of Sodium

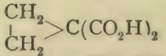
Pyrocinchonic Acid (Does not exist)

Pyrocinchonic Anhydride.

Hence, dimethyl and diethyl-maleïc acids cannot contain two carboxyl groups any more than carbonic acid can contain them. Even in the salts and esters a γ-lactone ring would be present. The hypothetical acid hydrates would be unsaturated γ-dioxy-lactones.

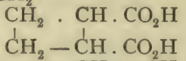
The cycloparaffin dicarboxylic acids, having a like carbon content and isomeric with the unsaturated dicarboxylic acids, will be discussed after the cycloparaffins, *e. g.*:

Trimethylene Dicarboxylic Acid,



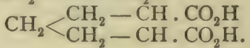
$$\genfrac{}{}{0pt}{}{CH_2}{CH_2}{>}C(CO_2H)_2$$

Tetramethylene Dicarboxylic Acid,



$$\genfrac{}{}{0pt}{}{CH_2\ .\ CH\,.\,CO_2H}{CH_2 - CH\,.\,CO_2H}$$

Pentamethylene Dicarboxylic Acid,



$$CH_2{<}\genfrac{}{}{0pt}{}{CH_2 - CH\,.\,CO_2H}{CH_2 - CH\,.\,CO_2H.}$$

The lowest member of the series has two possible structural isomerides: *methylene malonic acid*, $CH_2:C(CO_2H)_2$, and *ethylene dicarboxylic acid*, $CO_2HCH:CH\,.\,CO_2H$. The first is only known in the form of its ester. However, there are two acids, *fumaric* and *maleïc acids*, which it is customary to regard as different modifications of ethylene dicarboxylic acid.

(*a*) Alkylen Malonic Acids.

Methylene Malonic Ester, $CH_2:C{<}\genfrac{}{}{0pt}{}{CO_2C_2H_5}{CO_2C_2H_5}$, is produced when 1 molecule of methylene iodide and 2 molecules of sodium ethylate act upon 1 molecule of malonic ethyl ester (together with β-ethoxy-iso-succinic ester, $C_2H_5\,.\,O\,.\,CH_2\,.\,CH(CO_2R)_2$

(B. **23**, R. 194; **22**, 3294; A. **273**, 43, p. 486). Under diminished pressure it distils as a mobile, badly smelling oil. If allowed to stand, it soon changes to a white, solid mass, $(C_8H_{12}O_4)_2$. The liquid ester deports itself like an unsaturated compound. It unites with bromine. See also β-oxyisosuccinic acid, p. 486.

Ethidene Malonic Ester, $CH_3 . CH : C(CO_2C_2H_5)_2$, is formed by the condensation of malonic ester with acetaldehyde on heating with acetic anhydride (A. **218**, 145). It boils at 116° under a pressure of 17 mm. When saponified with baryta water it yields an oxydicarboxylic acid, $C_3H_5(OH)(CO_2H)_2$. It combines with malonic ester on heating, and becomes ethidene dimalonic ester.

The condensation of malonic ester with chloral may be effected by heating them with acetic acid anhydride, the product being the diethyl ester of *Trichlorethidene malonic acid*, $CCl_3 . CH : C(CO_2H)_2$, a thick oil, boiling about 160° under 23 mm. pressure. *Isopropylene Malonic Acid*, $(CH_3)_2C : C(CO_2H)_2$, melts at 170°. Its *ethyl ester*, boiling at 176° (120 mm.), is obtained from malonic ester and acetone by means of acetic anhydride (B. **28**, 785, 1122).

Allyl Malonic Acid, $CH_2 : CH . CH_2 . CH(CO_2H)_2$, is obtained from malonic ester by means of allyl iodide. It crystallizes in prisms and melts at 103° (A. **216**, 52). Compare γ-valerolactone, p. 344, and carbovalerolactonic acid, p. 494. See B. **29**, 1856, for *ethyl-allyl-malonic acid* and its homologues.

(*b*) *Unsaturated Dicarboxylic Acids, in which the carboxyl groups are attached to two carbon atoms* (p. 456).

Formation.—They can be obtained, like the acrylic acids, from the saturated dicarboxylic acids by the withdrawal of two hydrogen atoms. This is effected (1) by acting on the monobrom-derivatives with alkalies:

$$\underset{\text{Bromsuccinic Acid}}{C_2H_3Br(CO_2H)_2} + KOH = \underset{\text{Fumaric Acid.}}{C_2H_2(CO_2H)_2} + KBr + H_2O;$$

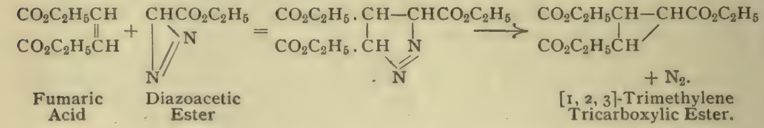
or the same result is reached (2) by letting potassium iodide act upon the dibrom-derivatives (p. 277). Thus, fumaric acid is formed from both dibrom- and isodibrom-succinic acids:

$$C_2H_2Br_2(CO_2H)_2 + 2KI = C_2H_2(CO_2H)_2 + 2KBr + I_2;$$

and mesaconic acid, $C_3H_4(CO_2H)_2$, from citra- and mesa-dibrom-pyrotartaric acids, $C_3H_4Br_2(CO_2H)_2$. As a general thing the unsaturated acids are obtained (3) from the oxydicarboxylic acids by the elimination of water (p. 458).

Deportment.—The acids of this series show the same tendency to addition reactions as was observed with the unsaturated monocarboxylic acids. Thus (1) hydrogen causes them to revert to saturated dicarboxylic acids; (2) haloid acids (particularly HBr) and (3) halogens convert them into haloid saturated dicarboxylic acids. (4) When heated with caustic potash an addition of hydrogen occurs with the production of monoxy-saturated dicarboxylic acids; others, again, are molecularly rearranged (B. **26**, 2082). Such rearrangement among isomerides has been induced by boiling water or acids (compare fumaric and maleïc acids, mesaconic, citraconic and itaconic acids). (5) Potassium permanganate oxidizes some of the unsaturated dicarboxylic acids to dioxy-dicarboxylic acids of the paraffin series. (6) Amido- and substituted amido-dicarboxylic acids of the saturated series have been obtained by the addition of ammonia, aniline and other bases.

(7) The acids of this series combine with diazoacetic acid, yielding pyrazoline derivatives (A. **273**, 214; B. **27**, 868), which pass into trimethylene derivatives by the elimination of nitrogen (p. 366):



Fumaric and maleïc acids, the first members of this series, are by far the most important acids of their class.

Fumaric Acid, $C_2H_2(CO_2H)_2$, occurs free in many plants, in Iceland moss, in *Fumaria officinalis* and in some fungi. It is formed (1) when inactive and active malic acid are heated (water and maleïc anhydride and other products) (B. **12**, 2281; **18**, 676); (2) in boiling the aqueous solutions of monochlor- and monobrom-succinic acids; (3) by heating dibrom- and isodibrom-succinic acids with a solution of potassium iodide; (4) synthetically from dichlor- or dibromacetic acid and silver malonate; (5) from maleïc acid (see the conversion of fumaric and maleïc acids into each other). It may be prepared by boiling brom-succinyl chloride with water (B. **23**, 3757).

Properties.—It is almost insoluble in cold water. It crystallizes from hot water in small, striated prisms. It sublimes at 200°, and at higher temperatures decomposes, forming maleïc anhydride and water.

The *silver salt*, $C_4H_2O_4Ag_2$, is very insoluble; it resists the light quite well. The *barium salt*, $C_4H_2O_4Ba + 3aq$, consists of prismatic crystals, which effloresce and when boiled with water change to $C_4H_2O_4Ba$—a salt that is practically insoluble in water.

The *esters* are obtained from the silver salt by the action of alkyl iodides, and by leading HCl into the alcoholic solutions of fumaric and maleïc acids (B. **12**, 2283). They are also produced in the distillation of the esters of brom-succinic acid, malic acid and aceto-malic acid (B. **22**, R. 813). They are also obtained from maleïc esters (see p. 459), and from diazoacetic esters on the application of heat (B. **29**, 763). They unite 2Br, forming esters of dibromsuccinic acid.

The *methyl ester*, $C_2H_2(CO_2 . CH_3)_2$, melts at 102°, and boils at 192°. The *ethyl ester* is liquid, and boils at 218° (B. **12**, 2283).

Many other substances have the power of adding themselves to them, *e.g.*, sodium acetoacetic ester, sodium malonic ester (B. **24**, 309, 2887, R. 636), sodium cyanacetic ester (B. **25**, R. 579), diazoacetic ester (p. 365) phenyl azoimide, etc.

Fumaryl Chloride, COCl . CH : CH . CO . Cl, boiling at 160°, is produced when PCl_5 acts upon fumaric acid (B. **18**, 1947). Bromine converts it into dibromsuccinyl chloride (A. Suppl. **2**, 86), and with sodium peroxide (hydrate) it yields *Fumaric Peroxide*, $C_4H_2O_4$, a white powder, exploding at 80° (B. **29**, 1726).

Fumaramic Acid, $CONH_2 . CH : CH . CO_2H$, melts at 217°. It is formed when asparagine is acted upon with methyl iodide and caustic potash (A. **259**, 137).

Fumaramide, $CONH_2CH = CH . CONH_2$, melts at 266° (B. **25**, 643).

Fumarhydrazide, $NH_2 . NH . CO . CH : CH . CO . NH . NH_2$, melts with decomposition at 220°. *Fumarazide* is crystalline. It explodes easily, and when boiled with alcohol yields *Fumarethyl urethane* (B. **29**, R. 231).

Fumaranilic Acid, $CONHC_6H_5CH = CH.CO_2H$, from the corresponding chloride and water, melts at 230–231°. *Fumaranilic Chloride*, $CONH.C_6H_5.CH = CH.COCl$, melting at 119–120°, crystallizes from ether in transparent, strongly refracting, sulphur-yellow colored prismatic needles or plates. It is produced when aniline acts upon fumaryl chloride in excess. *Fumardianilide*, $CONHC_6H_5CH = CHCONHC_6H_5$ (A. **239**, 144).

Maleïc Acid, $C_4H_4O_4$, melting at 130°, boils at 160° with decomposition into maleïc anhydride and water. Its anhydride is formed as mentioned under fumaric acid:

(1) By the rapid heating of malic acid.

(2) In the slow distillation of monochlor- and monobromsuccinic acid, as well as acetyl malic anhydride at the ordinary pressure.

(3) By the action of PCl_5 upon malic acid (A. **280**, 216).

(4) Maleïc acid is formed synthetically, in small amount, when silver or sodium acts upon dichloracetic acid and dichloracetic ester.

(5) Maleïc acid is obtained on decomposing trichlorphenomalic acid or β-trichloracetoacrylic acid (p. 382) with baryta water. Chloroform is produced at the same time.

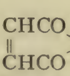
(6) From fumaric acid (see transformations of fumaric and maleïc acids).

Maleïc acid crystallizes in large prisms or plates, is very easily soluble in cold water, and possesses a peculiar, disagreeable taste.

Salts.—$C_4H_2O_4Ag_2$ is a finely divided precipitate. It gradually changes to large crystals. $C_4H_2O_4Ba + 1aq$ is soluble in hot water, and crystallizes well.

The *esters* result from the action of alkyl iodides upon the silver salt:

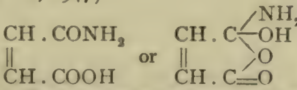
The *methyl ester*, $C_2H_2(CO_2.CH_3)_2$, is a liquid, and boils at 205°. The *ethyl ester* boils at 225°. When heated with iodine they change for the most part into fumaric esters.

Maleïc Anhydride, 

$\begin{matrix} CHCO \\ \| \\ CHCO \end{matrix} > O$

, melting at 53° and boiling at 202°, is produced (1) by distilling maleïc or fumaric acid alone, or more readily (2) with acetyl chloride; (3) by the distillation of monochlor- and monobromsuccinic acids, and also of aceto-malic anhydride (A. **254**, 155); (4) when PCl_5, P_2O_5 and $POCl_3$ act upon fumaric acid (A. **268**, 255). It is purified by crystallization from chloroform (B. **12**, 2281; **14**, 2546). It consists of needles or prisms, having a faintly penetrating odor. It regenerates maleïc acid by union with water, and forms isodibromsuccinic anhydride when heated with bromine.

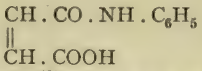
Maleïc Chloride (B. **18**, 1947).

Maleïnamic Acid, 

$\begin{matrix} CH.CONH_2 \\ \| \\ CH.COOH \end{matrix}$ or $\begin{matrix} CH.C{\lessgtr}^{NH_2}_{OH} \\ \| \quad\quad > O \\ CH.C{=}O \end{matrix}$

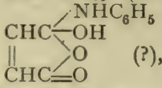
(?), melts at 152–153°. Its ammonium salt forms when ammonia acts upon maleïc anhydride. Aqueous potash converts the acid into maleïc acid, whereas fumaric acid results when it is treated with alcoholic potash. *Maleïnmethylamic Acid* melts at 149° (B. **29**, 653).

Maleïnanilic Acid,



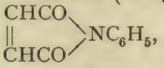
$$\begin{array}{l} CH\,.\,CO\,.\,NH\,.\,C_6H_5 \\ \| \\ CH\,.\,COOH \end{array}$$

or



(?), melting at 187–187.5°, is formed when aniline acts upon an ethereal solution of maleïc anhydride. Heated under greatly reduced pressure it splits into maleïc anhydride and aniline, which reunite in the receiver to maleïnanilic acid. Alcoholic potash and baryta water convert it into fumaric acid (A. **259**, 137).

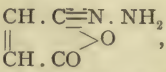
Maleïnanil,



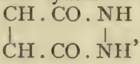
melting at 90–91°, results upon heating aniline malate. It consists of bright yellow needles. It combines readily with aniline, forming phenylasparaginanil (A. **239**, 154), melting at 210–211°.

Maleïnhydrazine, $CO_2H\,.\,CH:CH\,.\,CO_2N_2H_5$. See also dimethylketazine, p. 220.

Amidomaleïnimide,



, melting at 111°, is obtained from maleïc anhydride and hydrazine hydrate in alcohol. When its solution is heated it changes to *Maleïnhydrazide,*



$$\begin{array}{l} CH\,.\,CO\,.\,NH \\ | \qquad\qquad | \\ CH\,.\,CO\,.\,NH \end{array}$$

, consisting of little, white crystals, which do not melt at 250°. It is a strong acid.

BEHAVIOR OF FUMARIC AND MALEÏC ACIDS.

1. Acetylene is formed when the alkali salts of these acids are electrolyzed (p. 96).
2. Sodium amalgam, or zinc, reduces them both to succinic acid.
3. When heated to 100° with caustic soda both acids change to inactive malic acid (A. **269**, 76).
4. Fumaric and maleïc esters react with sodium alcoholates to form alkylic oxysuccinic acids (B. **18**, R. 536).
5. Bromine converts:

Fumaric acid	into dibromsuccinic acid.
Fumaric ester	" " " ester.
Fumaryl chloride	" " succinyl chloride.
Maleïc anhydride	" isodibromsuccinic anhydride.

6. Potassium permanganate changes (B. **14**, 713):

Fumaric acid	into racemic acid.
Maleïc "	" mesotartaric acid.

CONVERSION OF FUMARIC AND MALEÏC ACIDS INTO EACH OTHER.

1. When fumaric acid is heated, or treated with PCl_5, $POCl_3$ and P_2O_5 (A. **268**, 255; **273**, 31) it becomes maleïc anhydride.
2. Maleïc acid changes to fumaric acid:

(*a*) When it is heated alone in a sealed tube to 200° (B. **27**, 1365).

(*b*) By the action of cold HCl, HBr, HI and other acids; SO_2 and H_2S (B. **24**, R. 823), as well as by the action of bromine in sunlight (B. **29**, R. 1080).

(*c*) On heating maleïc ester with iodine fumaric esters result.

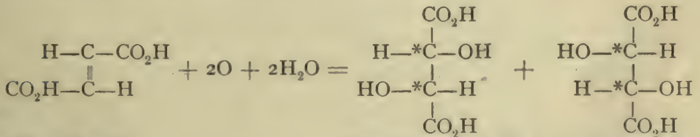
(*d*) Alcoholic potash changes maleïnamic and maleïnanilic acids to fumaric acid.

THE ISOMERISM OF FUMARIC AND MALEÏC ACIDS.

The view generally accepted as to the cause of the isomerism of these two acids was presented in the introduction, under the section relating to the geometrical isomerism, the stereoisomerism of the ethylene derivatives (p. 49). In conformity with this representation we find in maleïc acid, readily forming an anhydride, an atomic grouping, which follows the plane-symmetric configuration, according to which the carboxyl groups are so closely arranged with reference to each other that the production of an anhydride follows without difficulty. Fumaric acid is not capable of forming an anhydride, hence it has the central or axial symmetric structure.

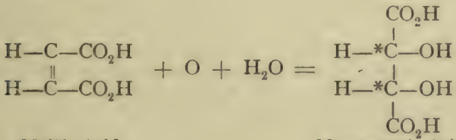
These space-formulas satisfactorily represent the intimate connection existing, as shown by Kekulé and Anschütz, between fumaric and racemic acids, and maleïc and inactive tartaric acids. According to the van t'Hoff-Le Bel view of these four acids, the oxidation of fumaric to racemic acid by means of potassium permanganate and maleïc to mesotartaric acid, may be shown by the following formulas, which have a spacial significance (compare p. 49):

2.



$$\begin{array}{c}H-C-CO_2H\\ \|\\ CO_2H-C-H\end{array} + 2O + 2H_2O = \begin{array}{c}CO_2H\\ |\\ H-{}^*C-OH\\ |\\ HO-{}^*C-H\\ |\\ CO_2H\end{array} + \begin{array}{c}CO_2H\\ |\\ HO-{}^*C-H\\ |\\ H-{}^*C-OH\\ |\\ CO_2H\end{array}$$

Fumaric Acid **Dextro-tartaric Acid + Lævo-tartaric Acid = Racemic Acid.**

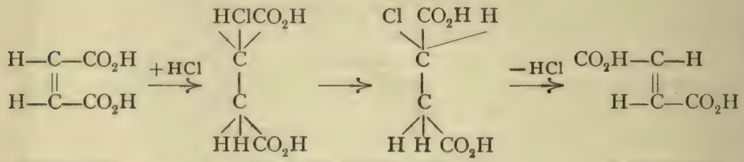


$$\begin{array}{c}H-C-CO_2H\\ \|\\ H-C-CO_2H\end{array} + O + H_2O = \begin{array}{c}CO_2H\\ |\\ H-{}^*C-OH\\ |\\ H-{}^*C-OH\\ |\\ CO_2H\end{array}$$

Malëic Acid **Mesotartaric Acid.**

The oxidation of the two acids, based on stereochemical formulas, is so represented that upon severing the double linkage in fumaric acid by the addition of hydroxyl groups an equal number of molecules of dextro- and lævo-tartaric acid results, while by the rupture of the double linkage in maleïc acid only mesotartaric acid is formed.

Cognizant of this view, J. Wislicenus has sought to explain the conversion of maleïc into fumaric acid by hydrochloric acid in the following manner: In these two acids the two doubly-linked carbon atoms cannot rotate independently of each other, consequently not in opposite directions, but when the double union is removed by the addition of two univalent atoms, then free rotation is restored. Accordingly, J. Wislicenus explains the conversion of maleïc acid by means of hydrochloric acid into fumaric acid as follows: Considering the extreme ease with which maleïc acid, in contrast to fumaric acid, lends itself to the formation of addition products (B. 12, 2282), it first absorbs the elements of the mineral acids (*e. g.*, HCl), and becomes a substituted succinic acid, which, under the directing influence of the greater affinities, assumes the preferred configuration (in which similar groups are as fully removed from each other as possible) by the rotation of the one system in opposition to the other, and now in consequence of the influence conditioned by the splitting-off of hydrochloric acid, due in part to the water present, and in part to the sparing solubility of fumaric acid, changes to this acid.



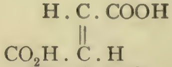
Maleïc Acid

Monochlorsuccinic Acid
previous to rotation
after rotation in the preferred position

Fumaric Acid.

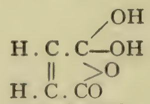
However, the intermediate product, monochlorsuccinic acid, is known in the free condition, that is, in the preferred configuration. It is stable toward hydrochloric acid at 10°, and its anhydride unites with water to the original acid, instead of yielding fumaric acid, although in so doing the monochlorsuccinic acid, as predicted by J. Wislicenus, in the conversion of maleïc into fumaric acid would change, through rotation, from the less favorable to the preferred configuration (Anschütz, A. **254**, 168). This is by no means the only fact with which the preceding explanation of the mechanism of the reactions showing the conversion of fumaric into maleïc acid, and vice versâ, clashes (compare B. **20**, 3306; **24**, R. 822; **24**, 3620; **25**, R. 418; **26**, R. 177; A. **259**, 1; **280**, 226).

In the introduction to the unsaturated dicarboxylic acids it was shown that at least some of these acids could only exist in the anhydride form, as their hydrate forms broke down in the moment of their liberation from salts into anhydrides and water. These acids are intimately related to maleïc acid; they are the dialkylic maleïc acids. The monoalkylic acids are still capable of existing in hydrate form, although they change more easily than maleïc acid to their anhydrides. Considering the analogy with carbonic acid, the salts of the dialkylic maleïc acids may be viewed as derivatives of a hypothetical acid hydrate, in which the two hydroxyl groups are attached to the same carbon atom, and this view may be considered to prevail with maleïc acid and with the monoalkylic maleïc acids, so similar to the dialkylic maleïc acids. The assumption that fumaric acid is symmetrical ethylene dicarboxylic acid and maleïc acid the γ-dioxylactone corresponding to this dicarboxylic acid in no wise renders a stereochemical formulation of the two acids impossible. Probably the stereochemical, different arrangement and the different position, in the chemical structure, of the atoms contained in both acids mutually influence each other (A. **254**, 168):



$$\begin{array}{c} H.C.COOH \\ \| \\ CO_2H.C.H \end{array}$$

Fumaric Acid



Maleïc Acid.

However, even this view, as yet, does not afford a satisfactory explanation of the reactions by which these acids are converted into each other. Consult A. **239**, 161, for the history of the isomerism of fumaric and maleïc acids.

The various ideas as to the cause of the isomerism of fumaric and maleïc acids are connected with the question as to the nature of the double linkage (p. 51).

Finally, attention may be directed to the difference in the heat of combustion of the acids. This would indicate that the energy present in the acids, in the form of atomic motion, is markedly different. "This fact suggests the possibility that the cause of the isomerism is not to be sought exclusively in the varying arrangement of the atoms, nor in their different spacial positions, but that we should also consider the varying magnitude of the motion of the atoms (or atom complexes)." It is also possible to imagine a case in which the isomerism would only be influenced by the difference in energy content—a case in which there might be perfect similarity in linkage and also in the spacial arrangement of the atoms."

In addition to structural and spacial isomerism, we would have the hypothesis of an *energy* or *dynamical isomerism* (Tanatar, A. **273**, 54; B. **11**, 1027; **29**, 1300), which would vastly more deserve this name than the views to which attention has been drawn in connection with the sym. dialkylic succinic acids (p. 444).

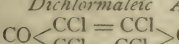
It is by no means established that fumaric acid is not a polymeric modification of maleïc acid. That their vapor densities are the same proves nothing on this point, inasmuch as the vapor densities of racemic and tartaric esters are identical, and yet the molecule of solid racemic acid consists of a molecule each of dextro- and lævotartaric acid. The same remarks are true in regard to the results obtained by the freezing-point depressions.

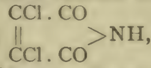
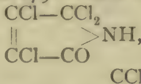
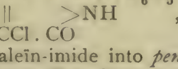
HALOID FUMARIC AND MALEÏC ACIDS.

Monochlorfumaric Acid, $C_4H_3ClO_4$, melting at 192°, results (1) from tartaric acid and PCl_5 or PCl_3; (2) from the two dichlorsuccinic acids; (3) from acetylene dicarboxylic acid and fuming nitric acid. *Monochlormaleïc Acid* melts at 106°; its *anhydride* melts at 0° and 34°, and boils at 197° (760 mm.), 95° (25 mm.). It is produced when acetyl chloride acts upon chlorfumaric acid, and when isodichlorsuccinic anhydride is heated (A. **280**, 222).

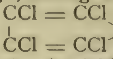
Brom-maleïc Acid, $C_4H_3BrO_4$, is produced by boiling dibromsuccinic acid with water. It melts at 128°. Its *anhydride*, boiling at 215°, results when isodibromsuccinic anhydride is heated alone, or by the action of acetic anhydride on dibromsuccinic acid. HBr converts it into dibromsuccinic acid and bromfumaric acid. **Brom-fumaric Acid**, $C_4H_3BrO_4$, is formed by boiling isodibromsuccinic acid, or by the addition of HBr to acetylene dicarboxylic acid. It melts at 179°.

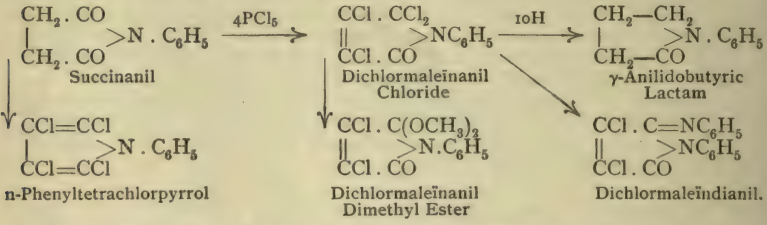
When heated alone, or upon boiling with acetyl chloride, both acids yield brommaleïc anhydride. *Mono-iodo-fumaric Acid* melts at 182–184° (B. **15**, 2697).

Dichlormaleïc Acid, $C_4Cl_2H_2O_4$, results when hexachlor-p-diketo-R-hexene,  $CO\left<\begin{matrix}CCl=CCl\\CCl_2-CCl_2\end{matrix}\right>CO$, and perchloracetylacrylic acid, $CCl_3CO.CCl=CCl.CO_2H$ (p. 382), are decomposed by caustic soda (A. **267**, 20; B. **25**, 2230). On the application of heat it passes into the *anhydride*, $C_2Cl_2(CO)_2O$, melting at 120°. PCl_5 converts succinic chloride into two isomeric *dichlormaleïc chlorides* (B. **18**, R. 184).

Its *imide*,  $\begin{matrix}CCl.CO\\ \| \\ CCl.CO\end{matrix}>NH$, is obtained when succinimide is heated in a current of chlorine. It melts at 179°. One molecule of PCl_5 changes the imide to *dichlormaleïn imide-chloride*,  $\begin{matrix}CCl-CCl_2\\ \| \\ CCl-CO\end{matrix}>NH$, melting at 147–148°; this combines with aniline to *dichlormaleïn imide-anil*,  $\begin{matrix}CCl.C=N.C_6H_5\\ \| \\ CCl.CO\end{matrix}>NH$, melting at 151–152°.

Two molecules of PCl_5 convert dichlormaleïn-imide into *pentachlorpyrrol*, C_4Cl_5N, boiling at 90.5° (10 mm.). *Dichlormaleïn-anil*, melting at 203°, is produced when dichlormaleïn anil chloride is boiled with glacial acetic acid or water.

Dichlormaleïn anil chloride, melting at 123–124°, boiling at 179° (11 mm.) is produced, together with *tetrachlor-v-phenyl pyrrol*,  $\begin{array}{l}\mathrm{CCl=CCl}\\ | \qquad\qquad >\mathrm{N\,.\,C_6H_5}\\ \mathrm{CCl=CCl}\end{array}$, melting at 93°, on treating succinanil with PCl_5. By reduction it yields δ-anilido butyric-lactam (see succinimide, p. 448). Alcohols convert it into dialkylic esters: *dichlormaleïn-anil-dimethyl ester*, melting at 110°; while with aniline it yields *dichlormaleïndianil*, melting at 186–187° (A. 295, 27):



Succinanil

Dichlormaleïnanil Chloride

γ-Anilidobutyric Lactam

n-Phenyltetrachlorpyrrol

Dichlormaleïnanil Dimethyl Ester

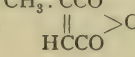
Dichlormaleïndianil.

Dibrom-maleïc Acid, $C_2Br_2(CO_2H)_2$, is obtained by acting on succinic acid with Br, or by the oxidation of mucobromic acid with bromine water, silver oxide or nitric acid. It is very readily soluble, melts at 120°–125°, and readily forms the *anhydride*, $C_2Br_2(CO)_2O$, which melts at 115° (B. 13, 736). *Chlorbrom-maleïc Acid*, see B. 29, R. 186.

Dibrom-fumaric Acid, melting at 219–222°, and *Di-iodofumaric acid*, decomposing at 192°, are the additive products of bromine and iodine with acetylene dicarboxylic acid (B. 12, 2213; 24, 4118).

Acids, $C_5H_6O_4 = C_3H_4(CO_2H)_2$.—Eight dicarboxylic acids, having this formula, are known. There are four unsaturated acids isomeric with ethidene malonic acid described on p. 457: (1) *Mesaconic acid*, (2) *Citraconic acid*, (3) *Itaconic acid*, (4) *Glutaconic acid*, and three trimethylene dicarboxylic acids. Mesaconic and citraconic acids bear the same relation to each other as fumaric to maleïc acid. They show similar conversions of one into the other. These, however, occur less readily than in the case of the latter acids (B. 29, R. 412). The introduction of the methyl group increases the tendency of citraconic acid very considerably to break down into its anhydride and water. This takes place at 100° under diminished pressure (compare chloral hydrate). Mesaconic acid is more easily changed by acetyl chloride to citraconic anhydride than fumaric acid to maleïc anhydride. Furthermore, maleïc anhydride combines more readily, and therefore more rapidly, with water than citraconic anhydride.

(1) **Mesaconic Acid**, Methyl Fumaric Acid, Oxytetrinic Acid, $C_3H_4(CO_2H)_2$, is prepared by heating citra- and itaconic acid with a little water to 200° and by evaporating citraconic acid with dilute nitric acid, conc. haloid acids, or with concentrated sodium hydrate (B. 269, 82; B. 29, 412) (Compare α- and β-methyl malic acid (p. 492) and from dibrommethyl acetoacetic acid (p. 378). *Brommesaconic Acid* melts at 220° (B. 27, 1851, 2130). It dissolves with difficulty in water and melts at 202°.

(2) **Citraconic Acid**, methyl maleïc acid, melting at 80° and easily soluble in water, is obtained from its anhydride by heating the latter with water. **Citraconic Anhydride**,  $\begin{array}{l}\mathrm{CH_3\,.\,CCO}\\ \quad\| \quad >\mathrm{O}\\ \mathrm{HCCO}\end{array}$, melting at 7° and boiling at 213–214°, is also formed by heat-

ing the acid and mesaconic acid, or on treating them with acetyl chloride, and is obtained by the repeated distillation of the distillate resulting from citric acid, due, probably, to a rearrangement of the itaconic anhydride produced at first.

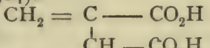
When boiled with a return condenser, it is changed in part to xeronic acid or diethylmaleïc anhydride, p. 466. *Bromcitraconic Anhydride* melts at 99° (B. **27**, 1855).

Hydrogen converts citra- and mesaconic acids into pyrotartaric acid (p. 444). Their haloid acid and halogen addition products have been described as halogen substitution products of pyrotartaric acid (p. 451). *Allylene*, $CH_3C \equiv CH$, results in the electrolysis of both acids.

Citraconanilic Acid melts at 153° (A. **254**, 135).

Citraconanil melts at 98° (B. **23**, 2979; **24**, 314).

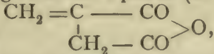
(3) *Itaconic Acid*, methylene succinic acid,



$$\begin{array}{l} CH_2 = C —— CO_2H \\ \qquad\quad | \\ \qquad\ CH_2 — CO_2H \end{array}$$

, melting at 161°, is formed by the union of its anhydride with water, or when citraconic anhydride is heated with 3–4 parts of water to 150°. Hydrogen causes it to revert to pyrotartaric acid, and when electrolyzed yields sym. allylene or allene, $CH_2 = C = CH_2$ (p. 99). It forms *pseudoitaconanilic acid*, the lactam of γ-anilidopyrotartaric acid (p. 492) (A. **254**, 129), when it is boiled with aniline. For the addition of HBr and Br_2 see p. 451. The *itaconic esters* readily polymerize to *vitreous modifications*, having high refractive power (B. **14**, 2787; A. **248**, 203).

Itaconic Anhydride,



$$\begin{array}{l} CH_2 = C —— CO \\ \qquad\ | \qquad\qquad\ \ \rangle O \\ \quad CH_2 — CO \end{array}$$

, melting at 68° and boiling at 139–140° (30 mm.), is probably the first decomposition product of aconitic acid, resulting from heating citric acid. The name aconitic acid gives rise to the name itaconic acid by syllable exchange. It has been obtained from its hydrate (B. **13**, 1539), and from the silver salt by the action of acetyl chloride (B. **13**, 1844). It has also been detected in the products formed in the distillation of citric acid (B. **13**, 1542). It crystallizes from chloroform in rhombic prisms, melts at 68°, and distils unaltered under diminished pressure, but at ordinary pressures changes to citraconic anhydride. It combines with water more readily than the latter. *Itaconanilic Acid* melts at 151.5° (A. **254**, 140).

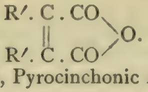
Homologues of Mesa-, Citra- and Itaconic Acids.

Before discussing glutaconic acid, the homologues of mesa-, citra-, and itaconic acids will be presented. The homologues of citraconic acid are produced when alkylic paraconic acids—the condensation products resulting from aldehydes and succinic acid, or pyrotartaric acid (p. 492)—are heated alone (A. **255**, 1; **283**, 47). The monoalkylic maleïc acids have yielded the homologues of mesaconic acid. *However, the dialkylic maleïc acids only exist as anhydrides in the free state, but can be converted, by boiling with concentrated caustic soda, into the corresponding dialkylic fumaric acids* (B. **29**, 1842). The conversion of certain itaconic acids into isomeric *aticonic acids* with caustic alkali is very remarkable. They seem to bear the same relation to each other that has been observed with fumaric and maleïc acids. The products of the action of alcoholic potash upon the dibrom-derivatives of the monoalkylic acetoacetic esters have been recognized as alkyl fumaric acids; thus, oxytetrinic acid is mesaconic acid, oxypentinic acid is ethyl fumaric acid, etc. (p. 379). Furthermore, monoalkylic fumaric acids have been obtained from monoalkylic ethane tricarboxylic acids by the elimination of halogen hydride and CO_2 after the halogens have been introduced (B. **24**, 2008).

Mono-alkylic Fumaric and Maleïc Acids:

	M. P.		M. P.		B. P.
Ethyl Fumaric Acid,	194°;	Ethyl Maleïc Acid,	100°;	Anhydride,	229°.
n-Propyl Fumaric Acid,	174°;	n-Propyl Maleïc Acid,	94°;	"	224°.
Isopropyl Fumaric Acid,	186°.				

Dialkylic Maleïc Anhydrides:



$$\begin{matrix} R'.C.CO \\ \| \\ R'.C.CO \end{matrix}\!\!>O.$$

(1) *Dimethylmaleïc Anhydride*, Pyrocinchonic Anhydride, melts at 96° and boils at 223°.

(2) *Methylethylmaleïc Anhydride* is a liquid boiling at 236–237°.

(3) *Diethylmaleïc Anhydride*, Xeronic Anhydride, is a liquid boiling at 242°.

Compounds 1 and 2 were obtained by heating the condensation product of succinic (or pyrotartaric) acid and pyroracemic acid to 130–140° with acetic anhydride until the evolution of CO_2 ceased (A. **267**, 204). Xeronic anhydride results when citraconic anhydride is heated with a return cooler. The three anhydrides are volatile in steam; they do not combine with water. Their hydrates cannot exist. They, however, form salts and esters (see p. 456).

Dimethyl Maleïc Anhydride, or Pyrocinchonic Anhydride, is obtained by oxidizing turpentine oil (together with terebic acid) with nitric acid; also by heating cinchonic acid:

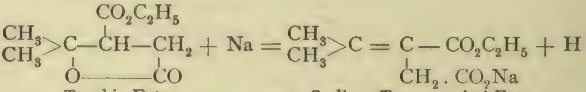
$$\begin{matrix} CH_2.CH(CO_2H).CH.CO_2H \\ CO{-}O{-}\!\!-\!\!-\!\!-CH_2 \end{matrix} \longrightarrow \begin{matrix} CH_3.C{=\!=\!=}C.CH_3 \\ CO{-}O{-}CO \end{matrix} + CO_2$$

Cinchonic Acid

Pyrocinchonic Anhydride.

and by heating α-dichlor-, or dibrom-propionic acid with reduced silver (B. **18**, 826, 835). Its aqueous solution has a very acid reaction and decomposes alkaline carbonates. Its solutions acquire a dark-red color on the addition of ferric chloride. It is reduced to 2-dimethyl succinic acids (p. 447), and with chlorine unites to dimethyl dichlor-succinic anhydride (B. **26**, R. 190). Pyrocinchonic acid, boiled with a 20 per cent. sodium hydrate solution, yields *dimethyl fumaric acid* or *methylmesaconic acid*, melting at 240°, and *α-methylitaconic acid*, melting at 150° (B. **29**, 1842).

Monoalkylic and dialkylic itaconic acids result from the action of sodium or sodium ethylate (A. **256**, 50) upon the corresponding paraconic esters (p. 492). Thus, terebic ester or γ-dimethyl paraconic ester with sodium or sodium ethylate yields teraconic acid or γ-dimethylitaconic acid:



$$\begin{matrix} & CO_2C_2H_5 & \\ {}^{CH_3}_{CH_3}\!>C{-} & CH{-} & CH_2 \\ O{-}\!\!-\!\!- & & CO \end{matrix} + Na = {}^{CH_3}_{CH_3}\!>C = \begin{matrix} C - CO_2C_2H_5 \\ CH_2.CO_2Na \end{matrix} + H$$

Terebic Ester

Sodium Teraconethyl Ester.

They are also produced when the mono-alkylic citraconic acids are heated to 140°–150° with water (B. **25**, R. 161; A. **256**, 99).

γ-Methylitaconic Acid, Ethidene Succinic Acid, $\begin{matrix} CH_3.CH = C - CO_2H \\ CH_2.CO_2H \end{matrix}$, melts at 165–166°. *α-Methylitaconic Acid* melts at 150° (see pyrocinchonic acid). *Ethylitaconic Acid* melts at 164–165°. n-*Propylitaconic Acid* melts at 159°. *Isobutylitaconic Acid* melts at 160–165°.

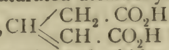
Teraconic Acid, γ-Dimethylitaconic Acid, $(CH_3)_2C:C<^{CO_2H}_{CH_2.CO_2H}$, is produced in small quantity (together with pyroterebic acid) (see this) in the distillation of terebic acid and by the condensation of succinic ester and acetone with sodium ethylate (B. **27**, 1122). It melts at 162°, decomposing at the same time into water and its anhydride, $C_7H_8O_3$. The latter boils near 275°. Hydrobromic acid or heat and sulphuric acid cause it to change to isomeric terebic acid (A. **226**, 363).

γ-Methyl-ethyl-itaconic Acid melts at 165° (A. **282**, 283).

Dimethylitaconic Acid, melting about 140°, is isomeric with teraconic acid, to which it seems to sustain the same relation as citraconic acid to mesaconic acid. It results on boiling teraconic acid with caustic soda (Fittig, B. **26**, 2082). *Methylethylitaconic Acid* melts at 141° (A. **282**, 283).

The following unsaturated dicarboxylic acids may also be mentioned:

Glutaconic Acid,



$CH{<}\begin{matrix}CH_2 . CO_2H\\ CH . CO_2H\end{matrix}$, melting at 132°, is isomeric with ita,- citra,- and mesaconic acids, and ethidene malonic acid; it arises in the saponification of the dicarboxyl glutaconic esters with hydrochloric acid (A. **222**, 249). It has also been obtained by the action of barium hydrate upon coumalic ester (p. 496) (A. **264**, 301). Its *zinc salt* separates from boiling solutions. The *ethyl ester*, from the silver salt, boils at 237–238°. The *anhydride*, produced by heating glutaconic acid and β-oxyglutaric acid (Kekulè), or by treating glutaconic acid with acetyl chloride, melts at 82–83° (m. p. 87°, B. **27**, 882). The *imide* melts at 183–184°. It is obtained (1) from glutaconamic acid, (2) from glutaconamide, and (3) from oxyglutaramide upon heating with sulphuric acid to 130–140°. Sodium and methyl iodide convert it into glutaconmethyl imide; nitrous acid produces an NO derivative; distilled over zinc dust it forms pyridine, and when treated with PCl_5, *pentachlorpyridine*, C_5Cl_5N (see constitution of pyridine), results.

β-Chlorglutaconic Acid melts at 195°; it is formed from PCl_5 and acetone dicarboxylic acid (see this); compare *glutinic acid* (p. 468). *Tetrachlorglutaconic Acid* melts at 109–110° (B. **25**, 2697). *Homologues of glutaconic acid*, see B. **23**, 3179; B. **27**, R. 193.

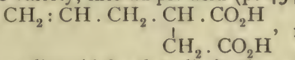
Hydromuconic Acids.

$\alpha\beta$-Acid: $CO_2H . \overset{\delta}{CH_2} . \overset{\gamma}{CH_2} . \overset{\beta}{CH} = \overset{\alpha}{CH} . CO_2H$, m. p. 169°—stable form.

$\beta\gamma$-Acid: $CO_2H . CH_2 . CH = CH . CH_2 . CO_2H$, m. p. 195°—unstable form.

The unstable modification is produced by the reduction of dichlormuconic acid, muconic acid (see below), and diacetylene dicarboxylic acid (p. 468). It dissolves with difficulty in cold water; potassium permanganate oxidizes it to malonic acid. It changes to the stable variety on boiling with sodium hydrate, and this permanganate oxidizes to succinic acid. Sodium amalgam reduces the unstable form, after its conversion into the stable variety, into adipic acid (p. 454).

Allyl Succinic Acid,

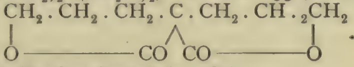


$\begin{array}{l}CH_2 : CH . CH_2 . CH . CO_2H\\ \qquad\qquad\qquad\;\; | \\ \qquad\qquad\qquad CH_2 . CO_2H\end{array}$, melts at 94°. It is formed from allyl ethenyl tricarboxylic acid by the elimination of CO_2 (B. **16**, 333). *Allylmethyl-* and *allylethyl succinic acids*, see B. **25**, 488.

Isovaleralglutaric Acid, $(CH_3)_2 . CH . CH_2 . CH : C(CO_2H)CH_2 . CH_2 . CO_2H$, formed together with di-isovaleral glutaric acid, melts at 75°.

C. DIOLEFINE DICARBOXYLIC ACIDS.

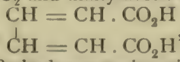
Diallylmalonic Acid, $(CH_2 = CHCH_2)_2C(CO_2H)_2$, melts at 133°, and with hydrobromic acid yields a dilactone,



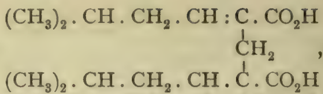
$$\begin{array}{ccccc} CH_2 . CH_2 . CH_2 & . & C & . & CH_2 . CH . {}_2CH_2 \\ | & & \wedge & & | \\ O\text{———} & & CO\;\;CO & & \text{———}O \end{array}$$

It breaks down into CO_2 and diallylacetic acid when heated (p. 289).

Muconic Acid,



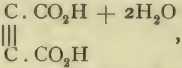
$\begin{array}{l}CH = CH . CO_2H\\ |\\ CH = CH . CO_2H\end{array}$, is formed when alcoholic potash acts upon the dibromide of $\beta\gamma$-hydromuconic acid. It melts at 260°. *Dichlormuconic Acid*, $C_6H_4Cl_2O_4$, results when PCl_5 acts upon mucic acid (B. **24**, R. 629). It yields $\beta\gamma$-hydromuconic acid with sodium amalgam (B. **23**, R. 232).

Di-isovaleralglutaric Acid, 

$$\begin{array}{r} (CH_3)_2.CH.CH_2.CH:C.CO_2H \\ \mid\quad\;\;\; \\ CH_2\quad\;\; \\ \mid\quad\;\;\; \\ (CH_3)_2.CH.CH_2.CH.C.CO_2H \end{array}$$

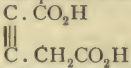
, melts at 220°, and is obtained from glutaric acid and isovaleraldehyde with acetic anhydride, sodium ethylate or sodium (A. **282**, 357).

D. ACETYLENE- AND POLYACETYLENE DICARBOXYLIC ACIDS.

Acetylene Dicarboxylic Acid, 

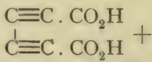
$$\begin{array}{l} C.CO_2H + 2H_2O \\ \parallel\!| \\ C.CO_2H \end{array}$$

, is obtained when aqueous or alcoholic potash is allowed to act upon dibrom- and isodibrom-succinic acid (A. **272**, 127). It effloresces on exposure. The anhydrous acid crystallizes from ether in thick plates, and melts with decomposition at 175°. The acid unites with the haloid acids to form halogen fumaric acids. With bromine and iodine it yields dihalogen fumaric acids (p 463). Its esters unite with bromine and form dibrommaleïc esters and dibromfumaric esters (B. **25**, R. 855). With water they yield oxalacetic ester (B. **22**, 2929). They combine with phenylhydrazine and hydrazine, forming the same pyrazolon derivatives as oxalacetic ester (B. **26**, 1719). And with diazobenzene-imide they form phenyltriazole dicarboxylic ester (B. **26**, R. 585). Oxalacetic ester and acetylene dicarboxylic ester are condensed by alcoholic potash to aconitic ester (B. **24**, 127). See acetoxymaleïc anhydride (p. 495). The primary *potassium salt*, C_4HKO_4, is not very soluble in water, and when heated decomposes into CO_2 and potassium propiolate (p. 287). The *silver salt* breaks down readily into CO_2 and silver acetylide (A. **272**, 139). The *diethyl ester*, boiling at 145–148° (15 mm.), is obtained from dibromsuccinic ester with sodium ethylate (B. **26**, R. 706). See also thiophene tetracarboxylic esters.

Glutinic Acid, 

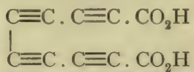
$$\begin{array}{l} C.CO_2H \\ \parallel\!| \\ C.CH_2CO_2H \end{array}$$

, is obtained by the action of alcoholic potash (B. **20**, 147) upon chlorglutaconic acid (p. 467). It melts at 145–146° with evolution of carbon dioxide.

Diacetylene Dicarboxylic Acid, 

$$\begin{array}{l} C\equiv C.CO_2H \\ \mid \\ C\equiv C.CO_2H \end{array} + H_2O$$

, is made by the action of potassium ferricyanide upon the copper compound of propiolic acid (B. **18**, 678, 2269). It assumes a dark red color on exposure to light, and at 177° explodes with a loud report. Sodium amalgam reduces it to hydromuconic acid, then to adipic acid and at the same time splits it up into propionic acid. The *ethyl ester* is an oil boiling at 184° (200 mm.). Zinc and hydrochloric acid decompose it and yield propargylic ethyl ether.

Tetra-acetylene Dicarboxylic Acid, 

$$\begin{array}{l} C\equiv C.C\equiv C.CO_2H \\ \mid \\ C\equiv C.C\equiv C.CO_2H \end{array}$$

. Carbon dioxide escapes on digesting the acid sodium salt of diacetylene dicarboxylic acid with water, and there is formed the sodium salt of diacetylene monocarboxylic acid, $CH\equiv C.-C\equiv CO_2Na$, which cannot be obtained in a free condition. When ferricyanide of potassium acts upon the copper compound of this acid, tetra-acetylene dicarboxylic acid is formed. This crystallizes from ether in beautiful needles, rapidly darkening on exposure to light and exploding violently when heated. Consult B. **18**, 2277, for an experiment made to explain the explosibility of this derivative.

V. TRIHYDRIC ALCOHOLS: GLYCEROLS AND THEIR OXIDATION PRODUCTS.

The trihydric alcohols, or glycerols, and those bodies which may be regarded as oxidation products of these, attach themselves to the dihydric alcohols (glycols) and their oxidation products.

The glycerols are obtained from the hydrocarbons by the substitution of three hydroxyl groups for three hydrogen atoms, linked to different carbon atoms. As the number of hydroxyl groups increases, the number of theoretically possible classes of glycerols, in contrast to the glycols, also becomes greater. These trihydric bodies are called glycerols after their most important representative. The number of possible classes of oxidation products also grows accordingly, and in the case of the trihydric alcohols that number is now 19. However, this chapter of organic chemistry has been more irregularly developed than that pertaining to the dihydric derivatives, and it may be said that the glycerols serve, even to a less degree than the glycols, as starting-out material for the preparation of the various classes belonging here, some of which are: dioxymonocarboxylic acids, monoxydicarboxylic acids, diketone-mono-carboxylic acids, mono-ketone-dicarboxylic acids, tricarboxylic acids.

Oxydialdehydes, oxydiketones, trialdehydes, aldehyde diketones and triketones are only slightly, if at all, represented. The same may be said of the oxyaldehyde ketones, oxyaldehydic acids, oxyketonic acids, aldehyde-carboxylic acids, and aldehyde-ketone-carboxylic acids.

1. TRIHYDRIC ALCOHOLS.

Glycerol stands at the head of this class, although it is not a triprimary alcohol, but rather a diprimary-secondary alcohol. The simplest imaginable triprimary alcohol would have the formula $CH(CH_2OH)_3$, and could be referred to trimethylmethane, $CH(CH_3)_3$, whereas glycerol is derived from propane, and considering the structure of the carbon nucleus, it is the simplest trihydric alcohol.

Although it may appear unnecessary to develop all the possible kinds of trihydric alcohols and their oxidation products, as was done with the glycols, yet the oxidation products theoretically possible from glycerol will be deduced. By enlarging this scheme we really construct a comparative review of the oxygen compounds, obtainable from methane, ethane, and propane.

It is also possible to tabulate the formulas of the oxygen derivatives of a hydrocarbon in such manner that the hydrogen atoms may be regarded as replaced, step by step, by hydroxyl groups, and we may indicate the number of hydrogen atoms attached to one carbon atom, which have been replaced by hydroxyl groups.*

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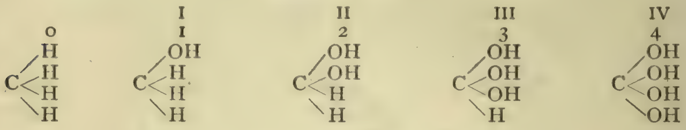
* This idea originated with A. v. Baeyer. It has the advantage that it facilitates the deduction of the possible hydroxyl derivatives of higher hydrocarbons, and determines the degree of oxidation, etc.

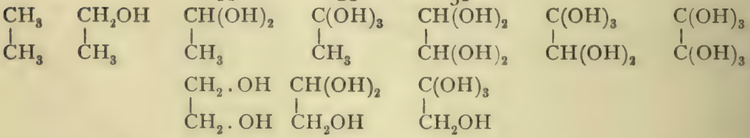
Thus, in compounds containing more than one hydroxyl attached to the same carbon atom, numbers are employed to express the formulas of ortho-derivatives, usually only stable in the form of ethers. When a carbon atom, of a hydrocarbon, is joined to hydrogen, and no hydrogen atoms are replaced by hydroxyl, this is expressed by a zero :

Methane = CH_4 : 0



Ethane = $CH_3 . CH_3$: 00

	I	II	III	IV	V	VI
00	10	20	30	22	32	33
		11	21	31		



$\begin{array}{c}CH_3\\|\\CH_3\end{array}$ $\begin{array}{c}CH_2OH\\|\\CH_3\end{array}$ $\begin{array}{c}CH(OH)_2\\|\\CH_3\end{array}$ $\begin{array}{c}C(OH)_3\\|\\CH_3\end{array}$ $\begin{array}{c}CH(OH)_2\\|\\CH(OH)_2\end{array}$ $\begin{array}{c}C(OH)_3\\|\\CH(OH)_2\end{array}$ $\begin{array}{c}C(OH)_3\\|\\C(OH)_3\end{array}$

$\begin{array}{c}CH_2 . OH\\|\\CH_2 . OH\end{array}$ $\begin{array}{c}CH(OH)_2\\|\\CH_2OH\end{array}$ $\begin{array}{c}C(OH)_3\\|\\CH_2OH\end{array}$

Propane = $CH_3 . CH_2 . CH_3$: 000

	I	II	III	IV	V	VI	VII	VIII
000	100	200	300	310	320	303	*322	323
	010	020	*210	301	*302	321	313	
		110	*201	220	311	*312		
		101	120	*202	*221	*222		
			111	211	*212			
				121				

The following formulas correspond to these groups of numbers :

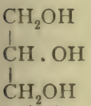
	000	$CH_3 . CH_2 . CH_3$	Propane
I :	100	$CH_2OH . CH_2 . CH_3$	n-Propyl Alcohol
	010	$CH_3 . CHOH . CH_3$	Isopropyl Alcohol
II :	200	$CH(OH)_2 . CH_2 . CH_3$	Propionic Aldehyde
	020	$CH_3C(OH)_2CH_3$	Acetone
	110	$CH_2(OH)CH . OH . CH_3$	Propylene Glycol
	101	$CH_2OH . CH_2 . CH_2OH$	Trimethylene Glycol
III :	300	$C(OH)_3 . CH_2 . CH_3$	Propionic Acid
	*210	$CH(OH)_2 . CH(OH)CH_3$	Unknown
	*201	$CH(OH)_2CH_2 . CH_2OH$	Unknown
	120	$CH_2OH . C(OH)_2CH_3$	Oxyacetone, Ketol
	111	$CH_2OH . CHOH . CH_2OH$	Glycerol
IV :	310	$C(OH)_3 . CHOH . CH_3$	Lactic Acid
	301	$C(OH)_3 . CH_2 . CH_2OH$	Hydracrylic Acid
	220	$CH(OH)_2 . C(OH)_2 . CH_3$	Pyroracemic Aldehyde
	*202	$CH(OH)_2 . CH_2 . CH(OH)_2$	Unknown
	211	$CH(OH)_2 . CH . OH . CH_2 . OH$	Glycerose
	121	$CH_2OH . C(OH)_2 . CH_2OH$	Dioxyacetone

---

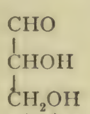
* Unknown.

V:	320	$C(OH)_3 . C(OH)_2 . CH_3$	Pyroracemic Acid
	*302	$C(OH)_3 . CH_2 . CH(OH)_2$	Unknown
	311	$C(OH)_3 . CHOH . CH_2OH$	Glyceric Acid
	*221	$CH(OH)_2 . C(OH)_2 . CH_2 . OH$	Unknown
	*212	$CH(OH)_2 . CH(OH) . CH(OH)_2$	Unknown
VI:	303	$C(OH)_3 . CH_2 . C(OH)_3$	Malonic Acid
	321	$C(OH)_3 . C(OH)_2 . CH_2OH$	Oxypyroracemic Acid
	*312	$C(OH)_3 . CHOH . CH(OH)_2$	Unknown
	*222	$CH(OH)_2 . C(OH)_2 . CH(OH)_2$	Unknown
VII:	322	$C(OH)_3 . C(OH)_2 . CH(OH)_2$	Unknown
	313	$C(OH)_3 . CH(OH) . C(OH)_3$	Tartronic Acid
VIII:	323	$C(OH)_3 . C(OH)_2 . C(OH)_3$	Mesoxalic Acid

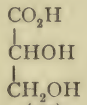
There are 29 imaginable hydroxyl substitution products of propane, and eleven of these should be regarded as oxidation products of glycerol, which will again be arranged together under their usual formulas—that is, their ortho- formulas minus water:


$CH_2OH-CH.OH-CH_2OH$

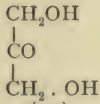
(111)
Glycerol


$CHO-CHOH-CH_2OH$

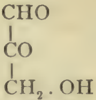
(211)
Glycerose


$CO_2H-CHOH-CH_2OH$

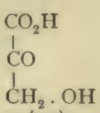
(311)
Glyceric Acid


$CH_2OH-CO-CH_2.OH$

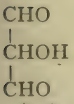
(121)
Dioxyacetone


$CHO-CO-CH_2.OH$

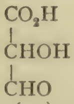
(221)
Unknown


$CO_2H-CO-CH_2.OH$

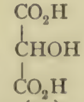
(321)
Oxypyroracemic Acid.


$CHO-CHOH-CHO$

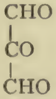
(212)
Unknown


$CO_2H-CHOH-CHO$

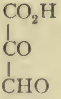
(312)
Unknown


$CO_2H-CHOH-CO_2H$

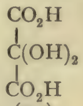
(313)
Tartronic Acid


$CHO-CO-CHO$

(222)
Unknown


$CO_2H-CO-CHO$

(322)
Unknown


$CO_2H-C(OH)_2-CO_2H$

(323)
Mesoxalic Acid.

Glyceric acid, tartronic acid, and mesoxalic acid are the only accurately known representatives of these eleven oxidation products of glycerol. The glyceroses and dioxyacetone have not been prepared in a pure state. Crude glycerose is a mixture of these two substances. Oxypyroracemic acid has received very little study.

Three hydrogen atoms in glycerol can be replaced by alcohol or acid radicals; the products are ethers and esters:

$$C_3H_5\left\{\begin{matrix}OH\\OH\\O.C_2H_3O\end{matrix}\right.\qquad C_3H_5\left\{\begin{matrix}OH\\O.C_2H_3O\\O.C_2H_3O\end{matrix}\right.\qquad C_3H_5\left\{\begin{matrix}O.C_2H_3O\\O.C_2H_3O\\O.C_2H_3O\end{matrix}\right.$$

Acetin Diacetin Triacetin.

The haloid esters are the halohydrins:

$C_3H_5(OH)_2Cl$ Monochlorhydrin $C_3H_5(OH)Cl_2$ Dichlorhydrin $C_3H_5Cl_3$ Trichlorhydrin.

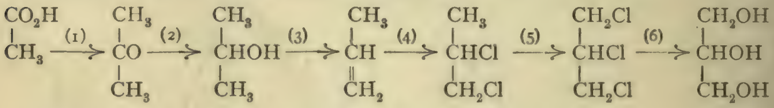
Formation.—The trihydric alcohols are obtained (1) by heating the bromides of the unsaturated alcohols with water; or—

(2) Upon oxidizing the unsaturated alcohols with potassium permanganate (B. **28**, R. 927).

Glycerol [Propantriol], $CH_2 . OH . CH . OH . CH_2OH$, is produced in small quantities in the alcoholic fermentation of sugar; hence is contained in wine. It is prepared exclusively from the fats and oils, which are glycerol esters of the fatty acids (p. 122). When the fats are saponified by bases or sulphuric acid, they decompose, like all esters, into fatty acids and the alcohol—glycerol.

Glycerol is also formed from synthetic glycerol trichloride by heating it with water to 170°, and from allyl alcohol when it is oxidized with potassium permanganate.

Historical—Scheele discovered glycerol in 1779, when he saponified olive oil with litharge, in making lead plaster. Chevreul, who recognized ester-like derivatives of glycerol in the fats and fatty oils, introduced the name glycerol, and in 1813 pointed to similarities between it and alcohol. The composition of glycerol was established in 1836, by Pelouze. Berthelot and Lucca (1853), and later Würtz (1855), explained its constitution, and proved that it was the simplest trihydric alcohol, the synthesis of which Friedel and Silva (1872) effected from acetic acid:



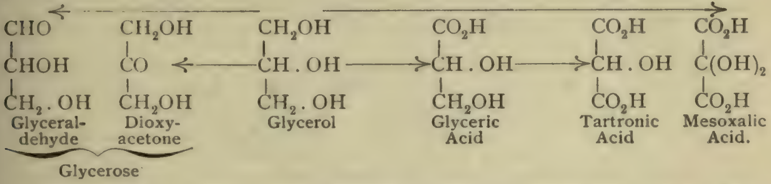
$$\begin{array}{c}CO_2H\\|\\CH_3\\\\\end{array} \xrightarrow{(1)} \begin{array}{c}CH_3\\|\\CO\\|\\CH_3\end{array} \xrightarrow{(2)} \begin{array}{c}CH_3\\|\\CHOH\\|\\CH_3\end{array} \xrightarrow{(3)} \begin{array}{c}CH_3\\|\\CH\\\|\\CH_2\end{array} \xrightarrow{(4)} \begin{array}{c}CH_3\\|\\CHCl\\|\\CH_2Cl\end{array} \xrightarrow{(5)} \begin{array}{c}CH_2Cl\\|\\CHCl\\|\\CH_2Cl\end{array} \xrightarrow{(6)} \begin{array}{c}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{array}$$

(1) Acetone is obtained from calcium acetate. (2) Acetone by reduction passes into isopropyl alcohol. (3) Propylene results when anhydrous zinc chloride withdraws water from isopropyl alcohol. (4) Chlorine and propylene yield propylene chloride. (5) Propylene chloride and iodine chloride unite to form propenyl trichloride or allyl trichloride, the trichlorhydrin of glycerol. (6) Glycerol is produced when trichlorhydrin is heated with much water to 160° (B. **6**, 969). Metallic iron and bromine convert propylene bromide into tribromhydrin, which silver acetate changes to triacetin. Bases saponify the latter and glycerol results (B. **24**, 4246).

Preparation.—At present glycerol is produced in large quantities in the manufacture of stearic acid; the fats are saponified by means of superheated steam, converting them directly into glycerol and fatty acids. In order to obtain a pure product the glycerol is again distilled under diminished pressure.

Properties.—Anhydrous glycerol is a thick, colorless syrup, of specific gravity 1.265 at 15°. Below 0° it solidifies to a white, crystalline mass, which melts at +17°. Under ordinary atmospheric pressure it boils at 290° (cor.) without decomposition; under 12 mm. at 170°. With superheated steam it distils entirely unaltered. It has a pure, sweet taste, hence the name glycerol. It absorbs water very energetically when exposed and mixes in every proportion with water and alcohol, but is insoluble in ether. It dissolves the alkalies, alkaline earths and many metallic oxides, forming with them, in all probability, metallic compounds similar to the alcoholates (p. 124).

Transformations.—(1) When glycerol is distilled with dehydrating substances, like sulphuric acid and phosphorus pentoxide, it decomposes into water and acroleïn (p. 208). It sustains a similar and partial decomposition when it is distilled alone. (2) When fused with caustic potash, it evolves hydrogen, and yields acetic and formic acids. (3) Platinum black, or dilute nitric acid, oxidizes it to glyceric and tartronic acids, while niter and bismuth nitrate change it to mesoxalic acid (B. **27**, R. 666). Under energetic oxidation the products are oxalic acid, glycollic acid, glyoxylic and other acids. (4) Moderated oxidation (with nitric acid or bromine) produces *glycerose*, which consists chiefly of glyceraldehyde and dioxyacetone, $CO(CH_2 . OH)_2$. This unites with CNH and forms trioxybutyric acid (B. **22,** 106; **23,** 387):



$$\begin{array}{cccccc} CHO & CH_2OH & CH_2OH & CO_2H & CO_2H & CO_2H \\ | & | & | & | & | & | \\ CHOH & CO \leftarrow & CH . OH \longrightarrow & CH . OH \longrightarrow & CH . OH & C(OH)_2 \\ | & | & | & | & | & | \\ CH_2 . OH & CH_2OH & CH_2 . OH & CH_2OH & CO_2H & CO_2H \\ \text{Glyceraldehyde} & \text{Dioxyacetone} & \text{Glycerol} & \text{Glyceric Acid} & \text{Tartronic Acid} & \text{Mesoxalic Acid.} \end{array}$$

(5) Phosphorus iodide or hydriodic acid converts it into allyl iodide, isopropyl iodide, and propylene (p. 113). (6) In the presence of yeast at 20–30° it ferments, forming propionic acid. By *schizomycetes fermentation*, induced by *Butyl bacillus* (B. **30,** 451), normal butyl alcohol (p. 125) and trimethylene glycol result (p. 295).

(7) When glycerol is distilled with ammonium chloride, ammonium phosphates and other ammonium salts, β-picoline, as well as 2 5-dimethyl pyrazine, results. Under certain conditions it is only the latter which is produced (B. **26,** R. 585; **24,** 4105; **27,** R. 436, 812).

Uses.—Glycerol is applied as such in medicine. It is also used as a lubricant in watches. Duplicating plates and hectographs consist of mixtures of gelatine and glycerol.

The bulk of glycerol is consumed in the manufacture of "nitroglycerine" (p. 474).

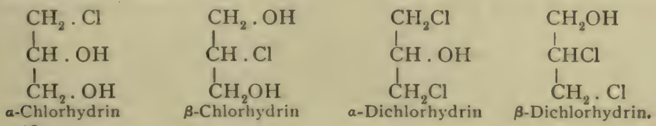
Glycerol Homologues.—1.2.3-*Butyl glycerol*, $CH_3 . CH(OH) . CH(OH) . CH_2OH$, boiling at 172–175° (27 mm.), is prepared from crotonylalcohol dibromide (p. 131).

[1.2.3-*Pentantriol*], $C_2H_5 . CH(OH) . CH(OH) . CH_2 . OH$, boils at 192° (63 mm.); [2.3.4-*Pentantriol*], $CH_3 . CH(OH) . CH(OH) . CH(OH) . CH_3$, boils at 180° (27 mm.); β-*Ethylglycerol*, $CH_3 . CH_2C(OH)(CH_2OH)_2$, boils at 186–189° (68 mm.). These and other glycerols result upon oxidizing unsaturated alcohols with potassium permanganate (B. **27,** R. 165; **28,** R. 927). *Penta-glycerol*, $CH_3C(CH_2 . OH)_3$, melts at 199°. It is obtained by the action of lime upon propyl aldehyde and formaldehyde (A. **276,** 76).

[1.4.5-*Hexantriol*], $CH_3 . CH(OH) . CH(OH) . CH_2 . CH_2 . CH_2OH$, boiling at 181° (10 mm.), and some other isomerides and higher homologues have been obtained from the addition products of bromine and hypochlorous acid with the corresponding unsaturated alcohols.

A. GLYCEROL ESTERS OF INORGANIC ACIDS.

(*a*) **Glycerol Haloid Esters.**—These are called halohydrins (p. 471). There are two possible isomeric mono- and di-halohydrins. They are distinguished as α-halohydrins and β-halohydrins:



$$\begin{array}{cccc} CH_2 . Cl & CH_2 . OH & CH_2Cl & CH_2OH \\ | & | & | & | \\ CH . OH & CH . Cl & CH . OH & CHCl \\ | & | & | & | \\ CH_2 . OH & CH_2OH & CH_2Cl & CH_2 . Cl \\ \alpha\text{-Chlorhydrin} & \beta\text{-Chlorhydrin} & \alpha\text{-Dichlorhydrin} & \beta\text{-Dichlorhydrin.} \end{array}$$

The monohalohydrins may also be regarded as halogen substitution products of propylene and trimethylene glycol, while the dihalohydrins are probably the dihalogen substitution products of propyl and isopropyl alcohol (p. 125).

a-Monohalohydrins are formed when the haloid acids act upon glycerol, and by the interaction of water and epihalohydrins. *a-Chlorhydrin*, $CH_2OH . CH . OH . CH_2Cl$, boils at 139° (18 mm.). *a-Bromhydrin* boils at 180° (10 mm.). *β-Chlorhydrin*, $CH_2OH . CHCl . CH_2OH$, boils at 146° (18 mm.). It is obtained from allyl alcohol and ClOH.

a-Dihalohydrins are produced when the haloid acids (A. **208**, 349) act upon glycerol, and upon the epihalohydrins (p. 477) (B. **10**, 557). Potassium iodide changes the chlorine derivative into the iodine compound (pp. 124, 126).

a-Dichlorhydrin, $CH_2Cl . CH . OH . CH_2Cl$, is a liquid, with ethereal odor, of sp. gr. 1.367 at 19°, and boils at 174°. It is not very soluble in water, but dissolves readily in alcohol and ether. When heated with hydriodic acid it becomes isopropyl iodide; sodium amalgam produces isopropyl alcohol. When sodium acts on an ethereal solution of *a*-dichlorhydrin, we do not get trimethylene alcohol, but allyl alcohol as a result of molecular transposition (B. **21**, 1289). Chromic acid oxidizes it to *β*-dichloracetone (p. 216) and chloracetic acid. Caustic potash converts it into epichlorhydrin (p. 477).

a-Dibromhydrin, $CH_2Br . CH(OH) . CH_2Br$, is an ethereal-smelling liquid, which boils at 219°; its sp. gr. at 18° is 2.11.

a-Di-iodhydrin is a thick oil of specific gravity 2.4, and solidifies at — 15°.

The *β-dihalohydrins* result from the addition of halogens to allyl alcohol.

β-Dichlorhydrin boils at 182–183°; its sp. gr. = 1.379 at 0°. Sodium converts it into allyl alcohol. Hydriodic acid changes it to isopropyl iodide. Fuming nitric acid oxidizes it to *aβ*-dichlorpropionic acid.

Both dichlorhydrins are changed to epichlorhydrin by the alkalies.

β-Dibromhydrin boils at 212–214°.

Trihalohydrins form when halogens are added to the allyl halides; also in the action of phosphorus haloids upon the dihalohydrins, and when iodine chloride acts upon propylene chloride, and bromine and iron upon propylene bromide and trimethylene bromide (B. **24**, 4246).

Trichlorhydrin, *Glyceryl Chloride*, 1.2.3-trichlorpropane, $CH_2Cl . CHCl . CH_2Cl$, boils at 158°.

Tribromhydrin fuses at 16°, and boils at 220°. Silver acetate converts it into glycerol triacetyl ester. When this is saponified it yields glycerol (p. 472).

(*b*) Glycerol Esters of the Mineral Acids Containing Oxygen.—The neutral nitric acid ester—*nitroglycerine* (discovered by Sobrero in 1847)—is the most important member of this class.

Nitroglycerine, glycerol nitrate, $CH_2(ONO_2) . CH(ONO_2) . CH_2(ONO_2)$, is produced by the action of a mixture of sulphuric and nitric acids upon glycerol. The latter is added, drop by drop, to a well-cooled mixture of equal volumes of concentrated nitric and sulphuric acids, as long as it dissolves; the solution is then poured into water, and the separated, heavy oil (nitroglycerine) is washed with water and dried by means of calcium chloride.

Nitroglycerine is a colorless oil, of sp. gr. 1.6, and becomes crystalline at —20°. It volatilizes very energetically at 160° (15 mm. pressure) (B. **29**, R. 41). It has a sweet taste, and is poisonous when taken inwardly. It is insoluble in water, dissolves with difficulty in cold alcohol, but is easily soluble in wood spirit and ether. Heated quickly, or upon percussion, it explodes very violently (*Nobel's explosive oil*); mixed with *kieselguhr* it forms *dynamite*, and with nitrocellulose, *smokeless powder*.

Alkalies convert nitroglycerine into glycerol and nitric acid; ammonium sulphide also regenerates glycerol. Both reactions prove that nitroglycerine is not a nitro-compound, but a nitric acid ester.

Glycerol-Nitrite, $C_3H_5(O\,.\,NO)_3$, is formed by the action of N_2O_3 upon glycerol. It is isomeric with *Trinitropropane* (B. **16**, 1697).

Glycerol-Sulphuric Acid, $C_3H_5\left\{\begin{matrix}(OH)_2\\ O\,.\,SO_3H\end{matrix}\right.$, is formed by mixing 1 part glycerol with 1 part of sulphuric acid.

Glycerol-Phosphoric Acid, $C_3H_5{<}\begin{matrix}(OH)_2\\ O\,.\,PO_3H_2\end{matrix}$, occurs combined with the fatty acids and choline as lecithin (see this) in the yolk of eggs, in the brain, in the bile, and in the nervous tissue. It is produced on mixing glycerol with metaphosphoric acid. The free acid is a stiff syrup, which decomposes into glycerol and phosphoric acid when it is heated with water. It yields easily soluble salts with two equivalents of metal. The calcium salt is more insoluble in hot than in cold water; on boiling its solution, it is deposited in glistening leaflets.

Glycerol *mercaptans* are produced when chlorhydrins are heated with alcoholic solutions of potassium sulphydrate.

B. GLYCEROL FATTY ACID ESTERS, GLYCERIDES.

(*a*) **Formic Acid Esters, Monoformin,** $C_3H_5(OH)_2OCHO$, is volatile under diminished pressure. It is supposed that it is formed on heating oxalic acid and glycerol. When it is heated alone it breaks down into allyl alcohol (p. 130), water, and carbon dioxide. Diformin is most certainly produced under these conditions. Monoformin also results from the action of a-monochlorhydrin upon sodium formate. **Diformin,** $C_3H_5(OH)\,.\,(O\,.\,CHO)_2$, boils at 163–166° (20–30 mm).

(*b*) **Acetic Esters,** or **Acetins,** result when glycerol and acetic acid are heated together: **Monacetin** at 100°; at 200°: **Diacetin,** $C_3H_5(O\,.\,COCH_3)_2(OH)$, boiling at 259–260° (B. **24**, 3466); at 250°: **Triacetin,** $C_3H_5(O\,.\,COCH_3)_3$, boiling at 258°, occurs in small quantities in the seed of *Evonymus europæus*, and has also been obtained from tribromhydrin (p. 476).

(*c*) **Tributyrin,** $C_3H_5(OC_4H_7O)_3$, occurs in cow's butter (p. 247).

(*d*) **Glycerides of Higher Fatty Acids** occur, as already represented (p. 249), in the vegetable and animal fatty oils, fats, and tallows. They can be artificially obtained by heating glycerol with the acids. They dissolve in alcohol with difficulty, but readily in ether. The fats are saponified when boiled with alkalies or lead oxide. The most important glycerides are:

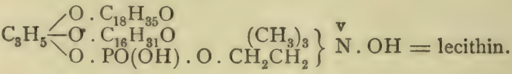
Trimyristin, or **Myristin,** $C_3H_5(O\,.\,C_{14}H_{27}O)_3$, Glycerol Myristic Ester, occurs in spermaceti, in muscat butter, and chiefly in oil nuts (from *Myristica surinamensis*), from which it is most readily obtained (B. **18**, 2011). It crystallizes from ether in glistening needles, melting at 55°. It yields myristic acid (p. 250) when saponified.

Tripalmitin, $C_3H_5(O\,.\,C_{16}H_{31}O)_3$, is found in most fats, especially in palm oil, from which it can be obtained by strong pressing.

Tristearin, $C_3H_5(O\,.\,C_{18}H_{35}O)_3$, occurs mainly in solid fats (tallows). It can be obtained by heating glycerol and stearic acid to 280–300°. It crystallizes from ether in shining leaflets, and melts at 71.5°. Its melting point is also lowered by repeated fusion.

Trioleïn, or **Oleïn,** $C_3H_5(O\,.\,C_{18}H_{33}O)_3$, is found in oils, like olive oil. It solidifies at —6°. It is oxidized on exposure to the air. Nitrous acid converts it into the isomeric elaïdin, which melts at 36° (p. 286).

Lecithins are widely distributed in the animal organism and occur especially in the brain, in the nerves, the blood corpuscles. and the yellow of egg, from which stearin-palmitic lecithin is most easily prepared. Lecithin occurs in the seeds of plants (B. **29**, 2761). It is a wax-like mass, easily soluble in alcohol and ether, and crystallizes in fine needles. It swells up in water and forms an opalescent solution, from which it is reprecipitated by various salts. It unites with bases and acids to salts, forming a sparingly soluble double salt, $(C_{42}H_{84}NPO_8\,.\,HCl)_2\,.\,PtCl_4$, with platinic chloride. Lecithin decomposes into choline, glycerol-phosphoric acid (see above), stearic acid, and palmitic acid, when it is boiled with acids or baryta water. Therefore we assume it to be an ethereal compound of choline with glycero-phosphoric acid, combined as glyceride with stearic and palmitic acids :



The distearin and dioleo- compounds are also known. *Protagon*, a substance obtained from the brain, appears to be closely related to the *lecithins.*

Glycerol Ethers : 1. Alkyl Ethers.

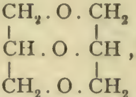
Mixed ethers of glycerol with alcohol radicals are obtained by heating the mono- and dichlorhydrins with sodium alcoholates:

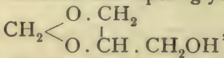
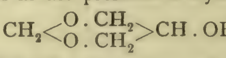
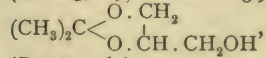
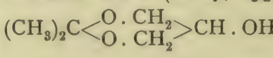
$$C_3H_5\left\{\begin{matrix}OH\\Cl_2\end{matrix}\right. + 2C_2H_5 . ONa = C_3H_5\left\{\begin{matrix}OH\\(O . C_2H_5)_2\end{matrix}\right. + 2NaCl.$$

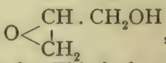
Monoethylin, $C_3H_5\left\{\begin{matrix}(OH)_2\\O . C_2H_5\end{matrix}\right.$, is soluble in water, and boils at 230°. **Diethylin,** $C_3H_5\left\{\begin{matrix}OH\\(O . C_2H_5)_2\end{matrix}\right.$, dissolves with difficulty in water, has an odor resembling that of peppermint, and boils at 191°. When its sodium compound is treated with ethyl iodide we obtain *Triethylin*, $C_3H_5(O . C_2H_5)_3$, insoluble in water and boiling at 185°.

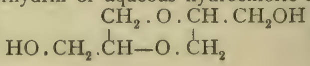
Allylin, $C_3H_5\left\{\begin{matrix}(OH)_2\\O . C_3H_5\end{matrix}\right.$, monoallyl ether, is produced by heating glycerol with oxalic acid (B. 14, 1946, 2270), and is present in the residue from the preparation of allyl alcohol (p. 130). It is a thick liquid, boiling at 225–240°. **Diallylin,** $HO . C_3H_5(OC_3H_5)_2$, boiling at 225–227°, is produced when sodium allylate acts upon epichlorhydrin (B. 25, R. 506).

2. Cyclic Ethers.

Glycerol Ether, 
$\begin{matrix}CH_2 . O . CH_2\\ | \quad\quad | \\ CH . O . CH\\ | \quad\quad | \\ CH_2 . O . CH_2\end{matrix}$, boiling at 169–172°, occurs together with allylin.

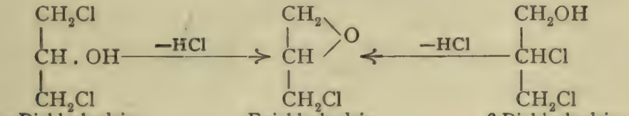
Glycerol derivatives, resembling the acetals, are produced when formaldehyde, benzaldehyde, or acetone acts upon glycerol in the presence of hydrochloric acid. *Formal glycerol*, 
$CH_2<\begin{matrix}O . CH_2\\ \quad | \\ O . CH . CH_2OH\end{matrix}$, or 
$CH_2<\begin{matrix}O . CH_2\\O . CH_2\end{matrix}>CH . OH$, boils at 193° (A. 289, 29). *Benzal glycerol* melts at 66° (B. 27, 1536). *Acetone Glycerol*, 
$(CH_3)_2C<\begin{matrix}O . CH_2\\ \quad | \\ O . CH . CH_2OH\end{matrix}$, or 
$(CH_3)_2C<\begin{matrix}O . CH_2\\O . CH_2\end{matrix}>CH . OH$, boils at 83° (11 mm.) (B. 28, 1169).

Glycide Compounds : Glycide, *Epihydrin Alcohol*, 
$O<\begin{matrix}CH . CH_2OH\\ | \\ CH_2\end{matrix}$, boiling at 162°, sp. gr. 1.165 (0°), is isomeric with acetyl carbinol. This body manifests the properties both of ethylene oxide and of ethyl alcohol. It is obtained from its acetate by the action of caustic soda or barium hydrate. Glycide and its acetate reduce ammoniacal silver solutions at ordinary temperatures.

Glycerol also forms *polyglycerols*. Thus glycerol yields **Diglycerol,** $(HO)_2 . C_3H_5OC_3H_5(OH)_2$, when it is treated with chlorhydrin or aqueous hydrochloric acid at 130°. The polymeride of glycide, *Diglycide*, 
$\begin{matrix} & CH_2 . O . CH . CH_2OH\\ & | \qquad\quad | \\ HO . CH_2 . & CH—O . CH_2\end{matrix}$ (?),

results from the action of sodium acetate upon epichlorhydrin in absolute alcohol, and the subsequent saponification of diglycide acetate with caustic soda.

Epichlorhydrin, $O<\begin{matrix}CH.CH_2Cl\\ | \\ CH_2\end{matrix}$, is isomeric with monochloracetone, and constitutes the starting-out material for the preparation of the glycide compounds. It is obtained from both dichlorhydrins by the action of caustic potash or soda (analogous to the formation of ethylene oxide from glycolchlorhydrin (p. 298):



α-Dichlorhydrin Epichlorhydrin β-Dichlorhydrin.

It is a very mobile liquid, insoluble in water, and boils at 117°. Its sp. gravity at 0° is 1.203. Its odor resembles that of chloroform, and its taste is sweetish and burning. It forms α dichlorhydrin with concentrated hydrochloric acid. PCl_5 converts it into trichlorhydrin. Continued heating with water to 180° changes it to α-monochlorhydrin. Concentrated nitric acid oxidizes it to β-chlorlactic acid. Metallic sodium converts it into sodium allylate, $CH_2 = CH.CH_2ONa$.

Like ethylene oxide, epichlorhydrin combines with CNH to the oxycyanide, $C_3H_5Cl<\begin{matrix}OH\\CN\end{matrix}$.

Epibromhydrin, C_3H_5OBr, from the dibromhydrins, boils at 130–140°.

Epi-iodohydrin, from epichlorhydrin and potassium iodide, boils at 160°.

Epiethylin, Ethyl Glycide Ether, $C_3H_5O \; O.C_2H_5$, boiling at 126–130°, and **amyl glycide ether,** $C_3H_5O.O.C_5H_{11}$, boiling at 188°, are produced on distilling the ethers corresponding to epichlorhydrin with caustic potash.

Acetic Glycide Ester, $C_3H_5O.O.C_2H_3O$, is produced by heating epichlorhydrin with anhydrous potassium acetate. It boils at 168–169°.

Nitrogen-containing Derivatives of Glycerols: Nitroisobutyl Glycol, $CH_3.C(NO_2).(CH_2OH)_2$, melting at 140°, is formed from nitroethane and formaldehyde (B. **28**, R. 774).

Triamino-propane, $CH_2NH_2.CH.NH_2.CH_2NH_2$, can be distilled without decomposition under reduced pressure. It is formed from the triazide of tricarballylic acid (compare p. 312). It is a syrupy liquid.

2. DIOXYALDEHYDES.

Glyceryl Aldehyde, [Propandiolal], $CH_2OH.CHOH.CHO$, and **Glycerol Ketone,** [Propandiolon], $CH_2OH.CO.CH_2OH$, are not known in a pure state. A mixture of them, called *glycerose*, is formed when glycerol is oxidized with dilute nitric acid or bromine. Caustic soda condenses it to *inactive acrose*, a compound related to grape sugar.

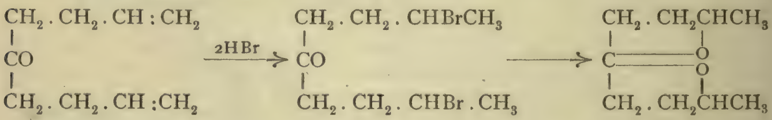
Nitromalonic Aldehyde, $NO_2CH(CHO)_2$, results from the action of alkaline nitrites upon mucobromic acid. It forms salts with the alkali metals and condenses to sym. trinitrobenzene, and with acetone to p-nitrophenol (B. **28**, 2597).

Chloral-aldol, $CCl_3.CH(OH).CH(CHO).CHOH.CH_3$, and **Butylchloral-aldol,** $CH_3 \; CHCl.CCl_2.CH(OH).CH(CHO).CHOH.CH_3$, are thick oils. They result from the condensation of chloral or butylchloral with paraldehyde and glacial acetic acid (B. **25**, 798).

3. DIOXYKETONES (OXETONES).

Dioxyacetone is the simplest possible dioxyketone. It is not known in a pure state. Its derivatives are: (1) Sym. **Diethoxyacetone**, $C_2H_5O . CH_2 . CO . CH_2 . OC_2H_5$, boiling at 195°, which is obtained from $\alpha\gamma$-diethoxy-acetoacetic ester as well as by the distillation of calcium ethyl glycollate (B. **28**, R. 295). It reduces Fehling's solution. (2) **Diamido-acetone**, $NH_2CH_2 . CO . CH_2NH_2$—the reduction product of di-isonitroso-acetone (B. **28**, 1519).

Fittig discovered the oxetones. They can be viewed as anhydrides of γ-dioxyketones. Their constitution follows from the formation of dimethyl-oxetone in the treatment of the dibrom- addition product of diallyl acetone (p. 221) with a potash solution (Volhard, A. **267**, 90):



$$\begin{array}{l} CH_2 . CH_2 . CH : CH_2 \\ | \\ CO \\ | \\ CH_2 . CH_2 . CH : CH_2 \end{array} \xrightarrow{2HBr} \begin{array}{l} CH_2 . CH_2 . CHBrCH_3 \\ | \\ CO \\ | \\ CH_2 . CH_2 . CHBr . CH_3 \end{array} \longrightarrow \begin{array}{l} CH_2 . CH_2CHCH_3 \\ |\qquad\qquad\quad | \\ C\text{———}O \\ \qquad\qquad\quad\; O \\ |\qquad\qquad\quad | \\ CH_2 . CH_2CHCH_3 \end{array}$$

The oxetones are obtained from the condensation products of the γ-lactones with sodium ethylate in consequence of the elimination of carbon dioxide (see p. 345).

Oxetone, $C_7H_{12}O_2$, boils at 159.4°. **Dimethyl Oxetone**, $C_9H_{16}O_2$, boils at 169.5°; sp. gr. 0.978 (0°). **Diethyl Oxetone**, $C_{11}H_{20}O_2$, boils at 209°. These oxetones are mobile liquids, and possess an agreeable odor. They are not very soluble in water, reduce an ammoniacal silver solution, and combine with 2HBr to γ-dibrom-ketones.

γ-**Pyrone**, $CO{<}{}^{CH\,=\,CH}_{CH\,=\,CH}{>}O$, may be considered the anhydride of an unsaturated dioxyketone.

4. OXYALDEHYDE KETONES.

Oxypyroracemic Aldehyde, $CHO . CO . CH_2OH$, is the simplest oxyaldehyde ketone. It is only known in the form of its osazone, melting at 134°, and is produced by the interaction of phenylhydrazine and dioxyacetone (B. **28**, 1522).

5. OXYDIKETONES.

α-**Dibromethyl Ketole**, $CH_3 . CBr_2COCH_2OH$, melting at 85°, and formed from brom-tetrinic acid and bromine, is a derivative of the simplest oxydiketone, $CH_3 . CO . CO . CH_2OH$.

Oxymethylene-Acetyl Acetone, $(CH_3CO)_2C = CHOH$, melting at 47° and boiling at 100° (20 mm.), 199° (ord. pressure), is a strong acid, stronger than acetic acid. It is soluble in aqueous alkaline acetates. It absorbs oxygen rapidly from the air, and when gently heated with water and mercuric oxide it decomposes into carbonic acid and acetyl acetone.

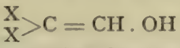
Its *copper salt* melts at 214°.

Etoxymethylene-Acetyl Acetone, $(CH_3 . CO)_2C = CHOC_2H_5$ (liquid, boiling at 141° under 16 mm.), results from the condensation of acetyl acetone with orthoformic ether. Water decomposes it into alcohol and the preceding body. Ammonia converts it into *amido-methylene acetyl acetone*, $(CH_3 . CO)_2C = CH . NH_2$, melting at 144°. With acetyl acetone it forms *methenyl-bisacetyl acetone*, $(CH_3 . CO)_2C = CH—CH (CO . CH_3)_2$, melting at 118°. Ammonia changes it to diacetyl-lutidine. By the withdrawal of water it becomes diacetyl metacresol.

Oxymethylene-acetyl acetone, as well as the corresponding derivatives of acetoacetic ester and malonic ester, can be considered as formic acid in which the intraradical oxygen has been replaced by a carbon atom carrying two negative groups (X):

$$O = CH.OH$$

Formic Acid



$$\begin{matrix}X\\X\end{matrix}\!>C = CH.OH$$

Oxymethylene Compounds.

As these bodies are strong monobasic acids, the group $X_2C =$ would seem to exert an influence upon the carbon atom combined with it, or upon the hydroxyl in union with the carbon atom, just as is done by oxygen that is joined with two bonds. It is true that the influence may not be so great as in the latter case. The compounds just described are the first of the complex substances, containing only C, H, and O, which, without carboxyl, still approach the monocarboxylic acids (formic excepted) in acidity. Indeed, in some instances they surpass them in this respect (B. **26**, 2731; privately communicated by L. Claisen).

6. ALDEHYDE DIKETONES.

The following are derivatives of the dialdehydes corresponding to mesoxalic acid (see this):

(1) **Diisonitrosoacetone**, $CH(N.OH).CO.CH(N.OH)$, melts at 144° with decomposition. It results when nitrous acid acts upon acetone dicarboxylic acid.

(2) **Trioximidopropane**, $CH(N.OH)C(N.OH).CH(N.OH)$, melting at 171°, is the result of the action of hydroxylamine upon diisonitrosoacetone (B. **21**, 2989).

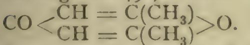
(3) **Propanon diphenyl hydrazone**, $C_6H_5NHN:CH.CO.CH:N.NHC_6H_5$, melting at 175°, with decomposition, is formed from acetone dicarboxylic acid and diazobenzene.

(4) **Propanon triphenylhydrazone**, melts at 166°. It consists of yellow leaflets. It results when the preceding body is treated at 120° with phenylhydrazine (B. **24**, 3259; **27**, 219).

7. TRIKETONES.

Pentantrion, $CH_3.CO.CO.CO.CH_3$, is the simplest triketone. It is only known in the form of a phenylhydrazine derivative of benzene azoacetyl acetone, $C_6H_5NH.N:C(COCH_3)_2$, which is produced when diazobenzene salts act upon sodium acetyl acetone (B. **25**, 746), and in that of an oxime, *isonitrosoacetyl acetone*, $HO.N:C(COCH_3)_2$ (B. **27**, R. 585).

Diacetyl Acetone, [2.4.6-*Heptantrion*], 2.4.4-*Trioxoheptan*, $CO(CH_2COCH_3)_2$, melting at 49°, results when baryta water acts upon 2.6-dimethylpyrone,



$CO\!<\!\begin{matrix}CH = C(CH_3)\\CH = C(CH_3)\end{matrix}\!>\!O$. Hydrochloric acid separates it from the barium salt. It decomposes spontaneously into water and dimethylpyrone (A. **257**, 276). Ferric chloride imparts a deep, dark red color to it. Its dioxime melts at 68°, and readily passes into an anhydride (B. **28**, 1817), melting with decomposition at 242°.

8. DIOXYMONOCARBOXYLIC ACIDS.

The acids of this series bear the same relation to the glycerols that the lactic acids sustain to the glycols. They can also be called dioxyderivatives of the fatty acids (p. 329). They may be artificially prepared by means of the general methods used in the production of oxyacids, and also by the oxidation of unsaturated acids with potassium permanganate (p. 330) (B. **21**, R. 660; A. **283**, 109).

Glyceric Acid, $C_3H_6O_4$ (dioxypropionic acid), [Propandiol Acid], is formed: (1) By the careful oxidation of glycerol with nitric acid (method of preparation, B. **9**, 1902; **10**, 267; **14**, 2071), or by oxidizing glycerol with mercuric oxide and baryta water (B. **18**, 3357), or with silver chloride and sodium hydroxide (B. **29**, R. 545). The calcium salt is decomposed with oxalic acid (B. **24**, R. 653):

$$CH_2(OH).CH(OH).CH_2(OH) + O_2 = CH_2(OH).CH(OH).CO.OH + H_2O.$$

(2) By the action of silver oxide upon β chlorlactic acid, $CH_2Cl.CH(OH).CO_2H$, and α-chlorhydracrylic acid, $CH_2(OH).CHCl.CO_2H$ (p. 341). (3) By heating glycidic acid with water (p. 481).

Glyceric acid forms a syrup which cannot be crystallized. It is easily soluble in water, alcohol, and acetone. It is optically inactive, but as it contains an asymmetric carbon atom (p. 45), it may be changed to active lævo-rotatory glyceric acid by the fermentation of its ammonium salt, through the agency of *Penicillium glaucum. Bacillus ethaceticus*, on the other hand, decomposes inactive glyceric acid so that the lævo-rotatory glyceric acid is destroyed and the dextro-rotatory acid remains (B. **24**, R. 635, 673).

Transformations.—When the acid is heated above 140° it decomposes into water, pyroracemic and pyrotartaric acids. When fused with potash it forms acetic and formic acids, and when boiled with it, yields oxalic and lactic acids. Phosphorus iodide converts it into β-iodpropionic acid. Heated with hydrochloric acid, it yields α-chlorhydracrylic acid and αβ-dichlorpropionic acid.

When glyceric acid is preserved a while, it probably forms a lactide or anhydride. This is sparingly soluble, and crystallizes in fine needles.

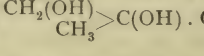
Its *calcium salt*, $(C_3H_5O_4)_2Ca + 2H_2O$, dissolves readily in water. The *lead salt*, $(C_3H_5O_4)_2Pb$, is not very soluble in water. The *ethyl ester* is formed on heating glyceric acid with absolute alcohol. The rotatory power of the optically active glyceric esters increases with the molecular weight (B. **26**, R. 540), and attains its maximum with the butyl ester (B. **27**, R. 137, 138).

The homologues of glyceric acid have been obtained (1) from the corresponding dibromfatty acids; (2) from the corresponding glycidic acids on heating them with water (A. **234**, 197); and (3) by oxidizing the corresponding unsaturated carboxylic acids (p. 281) with potassium permanganate (A. **268**, 8; B. **22**, R. 743).

There are three dioxybutyric acids:

(1) αβ-**Dioxybutyric Acid,** $CH_3.CH(OH).CH(OH).CO_2H$, β-**Methylglyceric Acid.** It melts at 74–75°.

(2) βγ-**Dioxybutyric Acid,** $CH_2(OH).CH(OH).CH_2.CO_2H$, is a thick oil.



(3) **Dioxyisobutyric Acid,** $\begin{matrix}CH_2(OH)\\CH_3\end{matrix}{>}C(OH).CO_2H$, α-methyl glyceric acid, melts at 100°.

γδ-**Dioxyvaleric Acid,** $CH_2(OH).CH(OH)CH_2.CH_2.CO_2H$, rapidly decomposes into water and an oxylactone. **Tigliglyceric Acid** melts at 88°, and **Angliglyceric Acid** melts at 111° (A. **283**, 109).

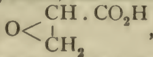
αβ-**Dioxyisoctylic Acid,** $(CH_3)_2CH.CH_2.CH_2.CH(OH)CH(OH)CO_2H$, melts at 106° (A. **283**, 291). α-**Isopropyl-β-isobutyl Glyceric Acid** melts at 154° (B. **29**, R. 508).

Dioxyundecylic Acid, $C_{11}H_{20}(OH)_2O_2$, from undecylenic acid, melts at 84–86°.

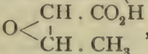
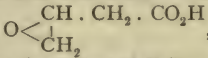
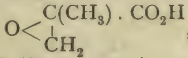
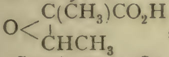
Dioxystearic Acid, $C_{18}H_{34}(OH)_2O_2$, from oleic acid, melts at 136°.

Dioxybehenic Acid, $C_{22}H_{42}(OH)_2O_2$, from erucic acid, melts at 136°.

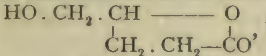
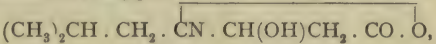
Glycidic Acids are obtained from the addition products of hypochlorous acid and unsaturated dicarboxylic acids, through the agency of alcoholic potash (A. **266**, 204). Like ethylene oxide, they take up the haloid acids, water, and ammonia, the products being chloroxyfatty acids or dioxyfatty acids, and amido-oxyfatty acids.

Glycidic Acid, *Epihydrinic Acid*,  $O<\begin{array}{l}CH\,.\,CO_2H\\ |\\ CH_2\end{array}$, is isomeric with pyroracemic acid. It is produced, like epichlorhydrin (p. 477), from α-chlorhydracrylic acid and β-chlorlactic acid by means of alcoholic potash. Glycidic acid, separated from its salts by means of sulphuric acid, is a mobile liquid miscible with water, alcohol, and ether. It is very volatile and has a piercing odor. The free acid and its salts are not colored red by iron sulphate solutions (distinction from isomeric pyroracemic acid). It combines with the haloid acids to β-halogen lactic acids, and with water, either on boiling or on standing, it yields glyceric acid. Its *ethyl ester*, obtained from the silver salt with ethyl iodide, melts at 162°.

It resembles malonic ester in its odor (B. **21**, 2053).

β-Methyl Glycidic Acid,  $O<\begin{array}{l}CH\,.\,CO_2H\\ |\\ CH\,.\,CH_3\end{array}$, is known in two modifications. The one melting at 84° unites to αβ-dioxybutyric acid with water. The other modification is a liquid. *Epihydrin-carboxylic Acid*,  $O<\begin{array}{l}CH\,.\,CH_2\,.\,CO_2H\\ |\\ CH_2\end{array}$, melting at 225°, is obtained from its nitrile, which results from the action of KCN upon epichlorhydrin (p. 477). *α-Methyl Glycidic Acid*,  $O<\begin{array}{l}C(CH_3)\,.\,CO_2H\\ |\\ CH_2\end{array}$, consists of shining leaflets. The *ethyl ester* boils at 162–164° (B. **21**, 2054). **αβ-Dimethyl Glycidic Acid**,  $O<\begin{array}{l}C(CH_3)CO_2H\\ |\\ CHCH_3\end{array}$, melts at 62° (A. **257**, 128). **ββ-Dimethyl Glycidic Acid.** See A. **292**, 282.

Oxylactones are obtained from some of the dioxyacids, which contain an hydroxyl group in the γ-position with reference to the carboxyl group:

Oxyvalerolactone,  $\begin{array}{l}HO\,.\,CH_2\,.\,CH ——— O\\ \quad | \qquad\qquad |\\ CH_2\,.\,CH_2—CO\end{array}$, boiling at 300–301°, results from the action of potassium permanganate (A. **268**, 61) upon allyl acetic acid. *Oxycaprolactone* and *Oxyisocaprolactone*, $C_6H_{10}O_3$, are colorless liquids, into which the oxidation products of hydrosorbic acid, by means of $KMnO_4$, rapidly pass on liberation from their barium salts (A. **268**, 34). *Oxyisoheptolactone*,  $(CH_3)_2CH\,.\,\overline{CH\,.\,CH(OH)\,.\,CH_2\,.\,COO}$, melts at 112°. *Oxyisoctolactone*,  $(CH_3)_2CH\,.\,CH_2\,.\,\underline{CN\,.\,CH(OH)CH_2\,.\,CO\,.\,O}$, melts at 33° (A. **283**, 278, 291).

Monamido-oxyacids: Serin, $CH_2(OH)\,.\,CH(NH_2)\,.\,CO_2H$, α-amidohydracrylic acid, is obtained by boiling serecin with dilute sulphuric acid. It forms hard crystals, soluble in 24 parts of water at 20°, but insoluble in alcohol and ether. Being an amido-acid it has a neutral reaction, but combines with both acids and bases. Nitrous acid converts it into glyceric acid.

Isomeric *β-amido-lactic acid*, $CH_2(NH_2)\,.\,CH(OH)\,.\,CO_2H$, is obtained from β-chlorlactic acid and glycidic acid by the action of ammonia (B. **13**, 1077). It dissolves with more difficulty in water than serin.

Homologues of the monoamido-oxyacids have been prepared by the union of homologous glycidic acids with ammonia.

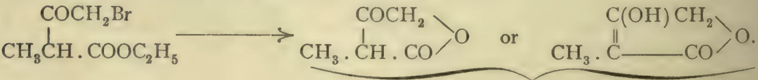
Diamido-carboxylic Acids.—*Diamidopropionic Acid*, $CH_2NH_2CHNH_2CO_2H$, has been obtained by the action of ammonia upon $\alpha\beta$-dibrompropionic acid. Other similar acids have been found in the decomposition products of the albuminoid bodies.

9. OXYKETONE CARBOXYLIC ACIDS.

Oxypyroracemic Acid, [Propanolon Acid], $CH_2OH.CO.CO_2H$, is formed when caustic soda acts upon collodion wool (B. **24**, 401). *Tribrommethylketol*, $CH_2OH.CO.CBr_3$. See tetronic acid.

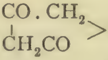
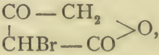
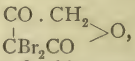
Ethoxyl-acetoacetic Ester, $CH_2.O.C_2H_5.CO.CH_2.COOC_2H_5$ or $CH_3CO.CH(OC_2H_5)CO_2C_2H_5$, boils at 105° (14 mm.). It is obtained by reducing ethoxyl chloracetoacetic ester, the condensation product from chloracetic ester and sodium.

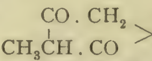
Demarçay acted with alcoholic caustic potash upon the γ-mono-brom-mono-alkylic acetoacetic esters and obtained *tetrinic acid* and its homologues, which may be regarded as γ-lactones of the oxyketone carboxylic acids:



Tetrinic Acid.

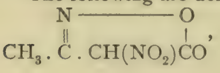
Michael was the first to declare that tetrinic acid was a lactone with the preceding formula. L. Wolff discovered the parent substance of tetrinic acid, and named it *tetronic acid*, after which tetrinic acid received the name *α-methyl tetronic acid* (A. **291**, 226). The salts of tetronic acid and the α-alkylic tetronic acids are derived from the hydroxyl formula isomeric with the ketone formula. The latter is preferred for the free acids.

Tetronic Acid,  $\begin{matrix}CO.CH_2\\ |\\ CH_2CO\end{matrix}\!\!>O$, melting at 141°, is produced when sodium amalgam acts upon *bromtetronic acid*,  $\begin{matrix}CO-CH_2\\ |\\ CHBr-CO\end{matrix}\!\!>O$, melting at 183°. This results when dibromacetoacetic ester is heated. *Dibromtetronic Acid*,  $\begin{matrix}CO.CH_2\\ |\\ CBr_2CO\end{matrix}\!\!>O$, is formed when bromine acts upon bromtetronic acid. It consists of white, readily soluble plates. It slowly decomposes at 174° with CO_2-evolution into *tribrommethylketol*, $CBr_3.CO.CH_2.OH$, and bromtetronic acid.

Tetrinic Acid, *α-Methyl Tetronic Acid*,  $\begin{matrix}CO.CH_2\\ |\\ CH_3CH.CO\end{matrix}\!\!>O$, melting at 189°, boils with partial decomposition at 292°. It results on heating γ-brom-methylacetoacetic ester or by treating it with alcoholic potash. Heated with water to 200°, it breaks down into ethyl ketol (p. 317) and CO_2, and when it is boiled with barium hydrate it yields glycollic acid and propionic acid. Chromic acid oxidizes it to diacetyl and CO_2 (A. **288**, 1).

Pentinic Acid, *α-Ethyltetronic Acid*, melts at 128°.
Hexinic Acid, *α-Propyltetronic Acid*, melts at 126°.
Heptinic Acid, *α-Isobutyltetronic Acid*, melts at 150°.

γ-Methoxyldimethylacetoacetic Ester, $CH_3O.CH_2.CO.C(CH_3)_2CO_2C_2H_5$, melts at 70° and boils at 241°. It is formed when methyl alcoholic sodium methylate acts upon γ-brom-dimethylacetoacetic ester (B. **30**, 856).

The following are derivatives of α-oxy-β-oxobutyric acid: *Nitromethylisoxazolon*,  $\begin{matrix}N & \text{———} & O\\ \Vert & & |\\ CH_3.C & .CH(NO_2) & CO\end{matrix}$, decomposing at 123°, results when oximidomethylisoxazolon is oxidized with nitric acid (B. **28**, 2093). *a-Amidoacetoacetic Ester*, $CH_3 . CO . CH . NH_2 . CO_2 . C_2H_5$, is produced in the reduction of isonitrosoacetoacetic ester with stannous chloride (B. **27**, 1142). *a-Isonitramineacetoacetic Ester*, $CH_3 . CO . CNa . (N_2O_2Na)CO_2 . C_2H_5$, is only known in the form of its sodium salt. This is produced when NO acts upon acetoacetic ester dissolved in alcohol in the presence of sodium ethylate (B. **28**, 1785); compare also isonitramine acetic acid, p. 361.

a-Hydroxylævulinic Acid, $CH_3 . CO . CH_2CH(OH)CO_2H$, melts at 103–104°, and *β-Hydroxylævulinic Acid*, $CH_3 . CO . CH(OH) . CH_2 . CO_2H$, is an oil. They are obtained from the corresponding bromlævulinic acids (A. **264**, 259).

Oxymethylene-acetoacetic ester, $HO . CH = C<^{CO_2C_2H_5}_{COCH_3}$, boiling at 95° (21 mm.), results, by the action of water, from *Ethoxymethylene Acetoacetic Ester*, $C_2H_5O . CH = C<^{CH_2 . C_2H_5}_{CO . CH_3}$, boiling at 149–150° (15 mm.). This is produced on heating the reaction product of orthoformic ester and acetoacetic ester with acetic anhydride (B. **26**, 2730). Oxymethylene acetoacetic ester is a strong acid (see oxymethylene acetylacetone, p. 478). It is readily soluble in alkaline acetates and insoluble in water. The *copper salt* melts at 156°. Ethoxymethylene acetoacetic ester and ammonia yield *amidomethylene acetoacetic ester*, $(C_6H_8O_3) = CH . NH_2$, melting at 55°, and it combines with acetoacetic ester to *methenylbisacetoacetic ester*, $(C_6H_8O_3) : CH . (C_6H_9O_3)$, melting at 96°. Ammonia changes the latter to lutidine dicarboxylic ester, while sodium methylate converts it into metaoxyuvitic acid (private communication from L. Claisen).

Ketoxystearic Acid, $CH_3[CH_2]_5CH[OH]CH_2 . CH_2 . CO[CH_2]_7CO_2H$. See ricinoleic acid, p. 286.

a-Mesityloxide Oxalic Acid (see olefine diketone carboxylic acids, p. 485).

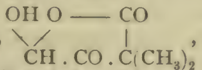
10. ALDEHYDOKETONE CARBOXYLIC ACIDS.

Glyoxyl Carboxylic Acid, $CHO . CO . CO_2H$, is not known. *Uric Acid* may be looked upon as the diureïde of this half-aldehyde of mesoxalic acid. *Di-isonitrosopropionic Acid*, $HO . N : CH . C : N(OH) . CO_2H$, is the dioxime of glyoxyl carboxylic acid. It is obtained from dibrompyroracemic acid. It is known in two modifications, the one melting at 143°, the other at 172° (B. **25**, 909). *Furazancarboxylic Acid*, $O<^{N : C . CO_2H}_{N : CH}$, melting at 107°, is the anhydride of this dioxime. It results from the oxidation of furazan-propionic acid with $KMnO_4$. Sodium hydroxide causes it to rearrange itself into cyanoximido-acetic acid (A. **260**, 79; B. **24**, 1167).

Muco-oxychloric acid and muco-oxybromic acid (A. **9**, 148, 160) are probably derivatives of an aldehydo-ketonic acid, $CHO . CH_2 . CO . CO_2H$, or of an unsaturated oxyaldehydic acid, $CHO . CH = C(OH)CO_2H$.

Glyoxylpropionic Acid, $HCO . CO . CH_2 . CH_2 . CO_2H$, is formed, along with diacetyl, when βδ-dibromlævulinic acid is boiled with water. It is a yellow crust. It passes into succinic acid upon oxidation. Its *oxime* is *γδ-dioximido-valeric acid*, $HC : N(OH) . C : N(OH) . CH_2 . CH_2 . CO_2H$, melting at 136°. Concentrated sulphuric acid changes it into the anhydride, *Furazanpropionic Acid*, $O<^{N : C . CH_2 . CH_2 . CO_2H}_{N : CH}$, melting at 86°. Sodium hydroxide converts this acid into *cyanoximidobutyric acid* (see this), while with potassium permanganate it yields furazancarboxylic acid.

Glyoxylisobutyric Acid, $CHO . CO . \overset{\overset{CO_2H}{|}}{C}(CH_3)_2$, melting at 138°, is obtained from the isomeric *dioxyacetyldimethyl acetic acid lactone*,

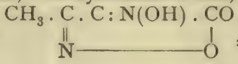


, melting at 168°, by repeated precipitation of its boiling alcoholic solution with water, or by its solution in soda and its immediate subsequent precipitation by hydrochloric acid.

The lactone was obtained on treating γ-methoxydimethyl acetoacetic ester with bromine, and then decomposing the mono-brom-substitution product with water (B. 30, 856).

II. DIKETONE CARBOXYLIC ACIDS.

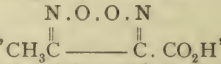
Paraffin Diketone Dicarboxylic Acids, *αβ*-**Diketo-** or *αβ*-**Dioxo-butyric Acid,** $CH_3 . CO . CO . CO_2H$. This acid is not known in a free condition. Two oximes are derived from it: *Isonitroso-acetoacetic Ester*, $CH_3 . CO . C : N(OH)CO_2C_2H_5$, melting at 53°, results when nitrous acid acts upon acetoacetic ester and acetomalonic ester (B. **20**, 1327). For an isomeric isonitroso-acetoacetic ester, see B. **28**, 2676; **29**, R. 997. *αβ*-**Di-isonitroso- or Dioximido-butyric Ester,** $CH_3 . C : N(OH) . C ; N(OH)CO_2C_2H_5$, decomposes at 152°. It results from the action of NH_2OH upon isonitroso acetoacetic ester (B. **25**, 2552). The free acid, known in two modifications, forms, with hydrochloric acid, a lactone-like anhydride—**Oximido-methyl-isoxazolon,**



$$\begin{array}{l}CH_3 . C . C : N(OH) . CO\\ \qquad \| \qquad\qquad\qquad\quad |\\ \qquad N\text{——————}O\end{array}$$

, decomposing at 132°.

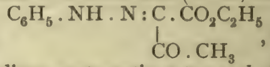
Peroxid-di-isonitrosobutyric Acid,



$$\begin{array}{l}\qquad N . O . O . N\\ \qquad \| \qquad\quad\ \ \|\\ CH_3C\text{———}C . CO_2H\end{array}$$

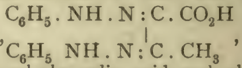
, melting at 92°, is produced when silver di-isonitrosobutyrate is oxidized with nitric acid (B. **28**, 2683).

Phenylhydrazone-acetyl-glyoxylic Ester,



$$\begin{array}{l}C_6H_5 . NH . N : C . CO_2C_2H_5\\ \qquad\qquad\qquad\ \ |\\ \qquad\qquad\qquad CO . CH_3\end{array}$$

, melting at 154°, is produced by the interaction of sodium acetoacetic ester and diazobenzene salts. **Osazone-acetyl-glyoxylic Acid,**



$$\begin{array}{l}C_6H_5 . NH . N : C . CO_2H\\ \qquad\qquad\qquad\ |\\ C_6H_5\ NH . N : C . CH_3\end{array}$$

, melting at 209°, is obtained from phenylhydrazone-acetyl-glyoxylic acid and phenylhydrazine in alcoholic solution (A. **247**, 205). *βγ*-**Diketo-** or *βγ*-**Dioxy-valeric Acid,** $CH_3 . CO . CO . CH_2 . CO_2H$. *β*-Isonitroso-lævulinic Acid, $CH_3CO . C : N(OH) . CH_2 . CO_2H$, may be referred to this acid, unknown in a free condition. It is obtained from acetosuccinic ester. It melts at 119°, decomposing into CO_2 and methyl-*β*-oximidoethyl ketone (p. 326).

Stearoxylic Acid and Behenoxylic Acid, already described (p. 288), are *α*-diketone carboxylic acids.

Acetyl Pyroracemic Acid Ester, Acetone Oxalic Ester, *αγ*-diketo- or *αγ*-dioxovalerianic ester, $CH_3 . CO . CH_2 . CO . CO_2C_2H_5$, results from the action of sodium ethylate upon acetone and oxalic ester. Ferric chloride imparts a dark red color to it. The free acid condenses to sym. oxytoluic acid, $CO_2H\ [1]\ C_6H_3\ [3.5](OH)CH_3$ (B. **22**, 3271). Acetone oxalic ester and phenylhydrazine yield a phenylpyrazole carboxylic ester, melting at 133° (A. **278**, 278).

The hydrogen in the acetoacetic esters can also be replaced by acid radicals. This is accomplished by acting upon the dry sodium compounds (suspended in ether) with acid chlorides. The products are diketone-monocarboxylic esters. Thus acetyl chloride (B. **17**, R. 604) produces:

Acetyl Acetoacetic Ester, $C_2H_3O . CH(C_2H_3O) . CO_2 . C_2H_5$, or **Diacetoacetic Ester,** boiling at 122–124° (50 mm.). Its ester is produced when alcohol acts upon the product obtained from $AlCl_3$ and acetyl chloride $(CH_3CO)_2CH . CCl_2OAlCl_2$ (p. 323) (Gustavson, B. **21**, R. 252). It is broken up by water, even at ordinary temperatures, into acetic acid and acetoacetic ester. Sodium ethylate displaces an acetyl group in it, forming acetoacetic ester and sodium acetoacetic ester.

Methyl diacetoacetic ester and ethyl diacetoacetic ester are only volatile without decomposition under diminished pressure.

Acetonyl Acetoacetic Ester, $CH_3 . CO . CH_2 . CH{<}\begin{matrix}CO_2C_2H_5\\ CO . CH_3\end{matrix}$, is produced by the action of chloracetone. $CH_3 . CO . CH_2Cl$, upon acetoacetic ester. It forms pyrotritaric ester (B. **17**, 2759) with fuming hydrochloric acid. On heating the ester with water to 160° C., acetonyl acetone results (p. 323).

Unsaturated Diketone Carboxylic Acids, *β-Mesityloxidoxalic Acid*, $\substack{CH_3 \\ CH_3}\!>\!C = CH.CO.CH_2.CO.CO_2H$, melts with decomposition at 166°. Caustic potash liberates it from either its *ethyl ether*, melting at 59° and boiling at 143° (11 mm.), or its *methyl ether*, melting at 67°. On allowing sodium in ether to act upon molecular quantities of mesityl oxide and oxalic ester, then acidulating with dilute sulphuric acid and distilling, a mixture of α- and β-mesityloxidoxalic esters results. It can be separated by means of a sodium carbonate solution, in which the *α-ether* alone is soluble. Ferric chloride turns this a blood red.

α-Mesityloxidoxalic Acid, $\substack{CH_3 \\ CH_3}\!>\!C = CH.CO.CH = C(OH)CO_2H$, melting at 92°, is obtained by the action of aqueous potash on its *ethyl ether*, melting at 21°, or its *methyl ether*, melting at 83° (A. **291**, 111, 137).

12. MONOXYDICARBOXYLIC ACIDS.

A. MONOXYPARAFFIN DICARBOXYLIC ACIDS, $C_nH_{2n-1}(OH)(CO_2H)_2$.

Numerous saturated monocarboxylic acids are known: thus, the oxymalonic acid group corresponds to the malonic acid group, oxysuccinic acid group to the ethyl succinic acid group, oxyglutaric acid group to the glutaric acid group, etc.

It may be mentioned here that there are many representatives of these acids in which the hydroxyl group occupies the γ-position with reference to the carboxyl group, and these acids, when separated from their salts, readily part with water and become lactones. In general, the alcoholic hydroxyl group is introduced into the dibasic acids, just as it is done in the case of the monobasic acids. The reaction leading to the alkylized paraconic acids (p. 492) is worthy of mention. It is a condensation reaction between aldehydes and succinic acid or monoalkylic succinic acids (p. 444).

OXYMALONIC ACID GROUP.

Tartronic Acid, $CH(OH)\!<\!\substack{CO_2H \\ CO_2H}$, *Oxymalonic Acid* [*Propanoldiacid*], is produced: (1) From glycerol by oxidation with potassium permanganate; (2) from chlor- and brom-malonic acid by the action of silver oxide or by saponifying their esters with alkalies; (3) from trichlorlactic acid when the latter is digested with alkalies (B. **18**, 754, 2852); (4) from dibrompyroracemic acid when digested with baryta water; (5) from mesoxalic acid by the action of sodium amalgam. (6) *Nucleus synthesis:* from glyoxylic acid by the action of CNH and hydrochloric acid, and by the spontaneous decomposition of nitrotartaric acid and dioxytartaric acid.

Its formation from nitro-tartaric acid, described in 1854 by Dessaignes, has given it the name tartronic acid.

Tartronic acid is easily soluble in water, alcohol, and ether, and crystallizes in large prisms. When pure, it melts at 184°, decomposing into carbon dioxide and polyglycollide, $(C_2H_2O_2)x$ (B. **18**, 756).

The *calcium salt*, $C_3H_2O_5Ca$, and *barium salt*, $C_3H_2O_5Ba + 2H_2O$, dissolve with difficulty in water, and are obtained as crystalline precipitates. The *ethyl ester*, $C_3H_2O_5(C_2H_5)_2$ (see above), is a liquid boiling at 222–225°. The *acetate*, $CH_3CO . OCH(CO_2C_2H_5)_2$, boils at 158–163° (60 mm.) (B. **24**, 2997).

Nitromalonic Ester, $NO_2 . CH(CO_2C_2H_5)_2$, is an oil (B. **23**, R. 62). *Dimethyl nitromalonamide*, $NO_2CH(CONHCH_3)_2$, melts at 156° (B. **28**, R. 912).

Fulminuric acid is also a derivative of nitromalonic acid (p. 238).

Amidomalonic Acid, $NH_2 . CH(CO_2H)_2$, consists of glistening prisms. It results from the reduction of oximidomalonic acid (see this). When its aqueous solution is heated, this body breaks down into CO_2 and glycin (p. 354). Its *amide*, $NH_2OH(CONH_2)_2$, warty crystals, is formed when alcoholic ammonia at 130° acts upon chlormalonic ester.

Imidomalonylamide, $NH[CH(CONH_2)_2]_2$ (B. **15**, 607) is produced at the same time. Its *nitrile*, $NH_2CH(CN)_2$, is a polymeride of prussic acid (p. 230).

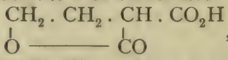
Alkylic Tartronic Acids.—*Methyl Tartronic Acid*, Isomalic Acid, α-oxyisosuccinic acid, $CH_3C(OH)(CO_2H)_2$, is obtained (1) by the action of silver oxide upon bromisosuccinic acid; (2) when prussic acid acts upon pyroracemic acid; (3) from diacetyl cyanide (p. 370) by the action of fuming hydrochloric acid (B. **26**, R. 7; **27**, R. 510). The acid breaks down into CO_2 and lactic acid when it is heated to 140°.

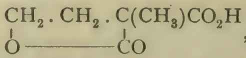
Ethyl Tartronic Acid, $C_2H_5C(OH)(CO_2H)_2$, is formed (1) on boiling ethyl chlormalonic ester with baryta water (p. 442); (2) from dipropionyl cyanide (p. 371); (3) by the action of ethyl iodide upon sodium acetartronic ester (B. **24**, 2999). It melts at 98°, and when heated higher breaks down into CO_2 and α-oxybutyric acid. *Propyl Tartronic Acid*, $CH_3 . CH_2 . CH_2 . C(OH) . (CO_2H)_2 + H_2O$, melts at 52–56°, and *Isopropyl Tartronic Acid* decomposes at 149°. They are formed by the saponification of dibutyryl and diisobutyryl dicyanide (p. 371).

α-Amidoisosuccinic Acid, $CH_3 . C(NH_2)(COOH)_2$, results when pyroracemic acid is acted upon with CNH and alcoholic ammonia (B. **20**, R. 507).

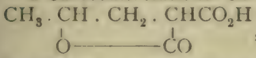
β-Oxyisosuccinic Acid, $CH_2OH . CH(CO_2H)_2$. Its *ethyl ether*, $C_2H_5OCH_2 . CH(CO_2H)_2$, has been obtained from methylene malonic ester (p. 456) by the action of alcoholic potash (B. **23**, R. 194).

γ-Oxyalkylic Malonic Acids.—The following γ-oxymalonic acids are only known in the form of alkali or alkaline earth salts. These are produced when the corresponding γ-lactone carboxylic acids are treated with caustic alkalies or the hydrates of the alkaline earths. The γ-lactonic acids can easily be got from these salts; these salts are produced by treatment with carbonates.

Butyrolactone-α-Carboxylic Acid,  $\begin{array}{l}CH_2 . CH_2 . CH . CO_2H \\ | \qquad\qquad\quad | \\ O\text{———}CO\end{array}$, is prepared from bromethyl malonic acid, $BrCH_2 . CH_2 . CH(CO_2H)_2$, melting at 117°. This is the hydrobromide addition product of vinaconic acid, the trimethylene-1-dicarboxylic acid, when it is heated with water; also on digesting the latter with dilute sulphuric acid (A. **227**, 13). Heated to 120°, butyrolactone carboxylic acid breaks down into CO_2 and butyrolactone (p. 345). The *phenyl ether* of *oxyethyltartronic acid*, $C_6H_5O . CH_2 . CH_2 . CH{<}\begin{smallmatrix}CO_2H \\ CO_2H\end{smallmatrix}$, melts at 142° (B. **29**, R. 286).

α-Methylbutyrolactone-α-carboxylic Acid,  $\begin{array}{l}CH_2 . CH_2 . C(CH_3)CO_2H \\ | \qquad\qquad\quad | \\ O\text{———}CO\end{array}$, melting at 98°, results when brom ethyl isosuccinic ester, the reaction product of ethylene bromide and sodium isosuccinic ester, is treated with baryta water and then acidulated (A. **294**, 89).

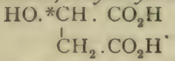
a-Carbovalerolactone Carboxylic Acid, γ-Methylbutyrolactone-a-carboxylic Acid,



$\begin{array}{l} CH_3 . CH . CH_2 . CHCO_2H \\ \quad O \text{———} CO \end{array}$, results when allyl malonic acid is acted upon with HBr. It breaks down at 200° into CO_2 and γ-valerolactone (p. 345).

OXYSUCCINIC ACID GROUP.

Malic Acid, *Oxyethylene Succinic Acid* (*Acidum malicum*), [*Butanol-diacid*],



$\begin{array}{l} HO.{}^*CH . CO_2H \\ CH_2 . CO_2H \end{array}$. Malic acid contains an asymmetric carbon atom; it can occur in three modifications: (1) a dextro-rotatory form, (2) a lævo-rotatory form, and (3) an inactive [d + l] variety. This is a compound of equal molecules of the dextro- and lævo-rotatory modifications.

The lævo-variety occurs free or in the form of salts in many plant juices, hence it is frequently spoken of as *ordinary* malic acid. It is found free in unripe apples, in grapes, and in gooseberries, also in mountain-ash berries (*Sorbus aucuparia*) and in *Berberis vulgaris*. It is obtained from the last two sources by means of the calcium salts (A. **38**, 257; B. **3**, 966). Acid potassium malate is contained in the leaves and stalks of rhubarb.

Historical.—Ordinary malic acid was discovered in 1785 by Scheele in unripe gooseberries. Liebig ascertained its composition in 1832. Pasteur, in 1852, obtained inactive malic acid from inactive aspartic acid, and Kekulé (1861) made it from bromsuccinic acid. The dextro-acid was first obtained by Bremer in the reduction of dextro-tartaric acid.

Formation of Optically Inactive or [d + l] *Malic Acid*, melting at 130° (B. **29**, 1698):

1. From the mono-ammonium salt of lævo-, and dextromalic acid.
2. By heating fumaric acid to 150–200° with water.
3. When fumaric or maleïc acid is heated with caustic soda to 100° (B. **18**, 2713).
4. By treating monobromsuccinic acid with silver oxide and water, with water alone, with dilute hydrochloric acid, or with dilute sodium hydroxide at 100° (B. **24**, R. 970).
5. By the action of N_2O_3 upon inactive aspartic acid.
6. By the reduction of racemic acid with hydriodic acid.
7. When oxalacetic ester is reduced with sodium amalgam in acid solution (B. **24**, 3417; **25**, 2448).
8. By the action of caustic potash upon the transposition-product of CNK and β-dichlorpropionic ester.
9. By saponifying the esters of chlorethane tricarboxylic acid.
10. When caustic potash acts upon γ-trichlor-β-oxybutyric acid, $CCl_3CH . OH . CH_2 . CO_2H$, the reaction-product of glacial acetic acid with chloral and malonic acid (B. **25**, 794).

The identity of the acids from 1 to 6 has been proved by means of the well-crystallized mono-ammonium salt, $C_4H_5O_5NH_4 + H_2O$, of the inactive acid (B. **18**, 1949, 2170).

Formation of the lævo- and dextro- forms: Racemic acid can be reduced to inactive malic acid, which cinchonine will resolve into salts of the two acids (B. **13**, 351; **18**, R. 537). The dextro-acid has also been obtained by the reduction of ordinary or dextro-tartaric acid with hydriodic acid, and by the action of nitrous acid upon dextro-aspartic acid, whereas l-asparagine and l-aspartic acid yield ordinary or l-malic acid (B. **28**, 2772). To convert the two optically active malic acids into each other it is only necessary to treat the chlorsuccinic acids, obtained from them, with moist silver oxide (Walden, B. **29**, 133).

Properties.—Malic acid forms deliquescent crystals, which dissolve readily in alcohol, slightly in ether, and melt at 100°.

Deportment.—Natural malic acid shows the following reactions: (1) When heated for some time to 140–150°, the principal product is fumaric acid; heated rapidly to 180°, it decomposes into water, fumaric acid, and maleïc anhydride (p. 459). (2) Succinic acid is formed by the reduction of malic acid. This is accomplished by the fermentation of the lime salt with yeast, or by heating the acid with hydriodic acid to 130° (p. 443). (3) When it is warmed with hydrobromic acid, it forms monobrom-succinic acid. PCl_5 at the ordinary temperature converts l-malic acid into d-chlorsuccinic acid, which moist silver oxide changes to d-malic acid. (4) Coumalic acid (p. 496) is produced when malic acid is heated alone or with sulphuric acid or zinc chloride. (5) The coumarines are produced when the acid is heated with phenols and sulphuric acid. This result is probably to be explained by assuming that the malic acid first changes to the half-aldehyde of malonic acid, $CHO.CH_2.CO_2H$, and this then condenses with the phenols (B. **17**, 1646).

Salts of the Inactive Acid: Mono-ammonium malate, $C_4H_5O_5NH_4 + H_2O$ (B. **18**, 1949, 2170). The *diethyl ester*, $C_2H_3(OH)(CO_2C_2H_5)_2$, boils at 255° (B. **25**, 2448).

Salts of the lævo-acid, malates: The *primary ammonium salt*, $C_4H_5(NH_4)O_5$, when exposed to a temperature of 160–200°, becomes *fumarimide*, $C_4H_2O_2.NH$ (A. **239**, 159 Anm.).

Neutral Calcium Malate, $C_4H_4O_5Ca + H_2O$, separates as a crystalline powder on boiling. The acid salt, $(C_4H_5O_5)_2Ca + 6H_2O$, forms large crystals which are not very soluble in cold water (B. **19**, R. 679).

Sodium Brommalate (from the acid, $C_4H_5BrO_5$) is formed when the aqueous solution of sodium dibromsuccinate is boiled; milk of lime transforms it into tartaric acid.

l-*Malic Ethers and Esters:* The dialkylic esters when slowly heated pass into fumaric esters (B. **18**, 1952), while PCl_5 and PBr_5 changes them, in chloroform, to d-chlor- and d-brom-succinic esters (p. 451).

The optical rotatory power of some of these esters has been determined. They are lævorotatory (B. **28**, R. 725; **29**, R. 164, C. 1897, I, 88):

l-Malic Methyl Ester	boils 122° (12 mm.);	$\alpha[D] = -6.883$,	$M[D] = 11.15$
l-Malic Ethyl Ester	“ 129° (12 mm.);	$\alpha[D] = -10.645$,	$M[D] = 20.22$
l-Malic-n-propyl Ester	“ 150° (12 mm.);	$\alpha[D] = -11.601$,	$M[D] = 25.29$
l-Malic-n-butyl Ester	“ 170° (12 mm.);	$\alpha[D] = -10.722$,	$M[D] = 26.38$

Triethyl Ester, $C_2H_5O.C_2H_3(CO_2C_2H_5)_2$, boils at 118–120° (15 mm.) (B. **13**, 1394).

Acetyl Malic Acid, $CH_3CO.OC_2H_3(CO_2H)_2$, melts at 132°.

Acetyl Malic Dimethyl Ester, $CH_3CO.OC_2H_3(CO_2CH_3)_2$, when carefully distilled at the ordinary temperature, yields fumaric dimethyl ester. *Acetyl Malic Anhy-*

dride, $CH_3 . CO . OC_2H_3(C_2O_3)$, melting at 53–54° and boiling at 160–162° (14 mm.), decomposes when distilled at the ordinary temperature into maleïc anhydride and acetic acid (A. **254**, 166).

Acetyl-l-malic methyl ester boils at 132° (12 mm.); $a[D] = -22.864$, $M[D] = -46.64$.

Acetyl-l-malic ethyl ester boils at 141° (12 mm.); $a[D] = -22.601$, $M[D] = -52.43$.

Propionyl-l-malic methyl ester boils at 142° (12 mm.); $a[D] = -23.08$, $M[D] = -50.31$.

Amides of Lævo-malic Acid: **Ethyl Malamate**, $C_2H_3(OH)<\begin{matrix} CO . NH_2 \\ CO_2 . C_2H_5 \end{matrix}$, is obtained by leading ammonia into the alcoholic solution of malic ester; it forms a crystalline mass.

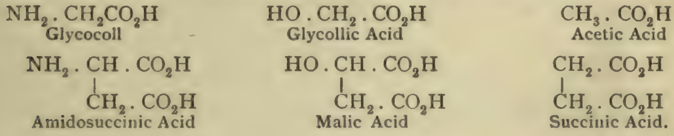
Malamide, $C_4H_8O_3N_2$, is formed by the action of ammonia upon dry ethyl malate.

Sulphosuccinic Acid, $(SO_3H)C_2H_3(CO_2H)_2$.

l-*Chlormalic Ethyl Ester*, melting at 162–165° (15 mm.), and l-*brommalic ethyl ester*, boiling at 165–168° (15 mm.), are produced when PCl_5 and PBr_5 act upon d-tartaric acid (B. **28**, 1291).

AMIDO-SUCCINIC ACIDS.

Aspartic acid bears the same relation to malic and succinic acids as glycocoll bears to glycollic acid and acetic acid; hence, it may be called amido-succinic acid:



$NH_2 . CH_2CO_2H$ Glycocoll	$HO . CH_2 . CO_2H$ Glycollic Acid	$CH_3 . CO_2H$ Acetic Acid
$\begin{array}{l} NH_2 . CH . CO_2H \\ \quad\;\; \vert \\ \quad\;\; CH_2 . CO_2H \end{array}$ Amidosuccinic Acid	$\begin{array}{l} HO . CH . CO_2H \\ \quad\;\; \vert \\ \quad\;\; CH_2 . CO_2H \end{array}$ Malic Acid	$\begin{array}{l} CH_2 . CO_2H \\ \vert \\ CH_2 . CO_2H \end{array}$ Succinic Acid.

Amidosuccinic acid contains an asymmetric carbon atom. Like malic acid, it can appear in three modifications. The l-amido-succinic acid or lævo-aspartic acid is the most important of these.

Inactive [d + l] Aspartic Acid, Asparacemic Acid, $NH_2C_2H_3(CO_2H)_2$, is produced:

(1) By the union of l- and d-aspartic acids.

(2) On heating active aspartic acid (*a*) with water, (*b*) with alcoholic ammonia to 140–150°, or (*c*) with hydrochloric acid to 170–180° (B. **19**, 1694).

(3) When fumarimide (p. 488) is boiled with hydrochloric acid.

(4) On heating fumaric and maleïc acids with ammonia (B. **20**, R. 557; **21**, R. 644).

(5) By evaporating a solution of hydroxylamine fumarate (B. **29**, 1478).

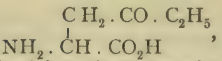
(6) By reducing oximido-succinic ester with sodium amalgam (B. **21**, R. 351).

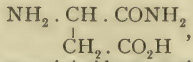
Like glycocoll, it combines with alkalies and acids yielding salts.

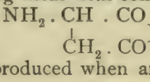
Nitrous acid changes it to inactive malic acid.

[d + l]-*Diethyl Aspartic Ester*, $NH_2 . C_2H_3(CO_2C_2H_5)_2$, boiling at 150–154° (25 mm.), is produced on heating fumaric and maleïc esters with alcoholic ammonia (B. **21**, R. 86).

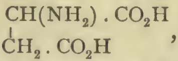
Ethyl a-Aspartic Ester, $NH_2 . \begin{array}{l} CH . CO_2C_2H_5 \\ \vert \\ CH_2 . CO_2H \end{array}$, melting at 165° (decomposition), is formed by the reduction of *a*-oximido-succinic monethyl ester and the diethyl oximido-oxalacetic ester. Ammonia converts it into *inactive a*-asparagine (constitution, compare p. 491).

Ethyl β-Aspartic Ester,  $\begin{array}{l} \quad CH_2 . CO . C_2H_5 \\ NH_2 . CH . CO_2H \end{array}$, melts with decomposition at about 200°, and is also obtained from the oxime of oxalacetic ester by reduction with sodium amalgam. A partial saponification occurs at the same time. Ammonia converts it into the two *optically active asparagines*, which are therefore β-amidosuccinamic acids.

[d + l] *a*-**Asparagine**,  $\begin{array}{l} NH_2 . CH . CONH_2 \\ \quad CH_2 . CO_2H \end{array}$, decomposes at 213–215° without melting, and results from asparaginimide, aspartic diethyl ester, and *a*-aspartic monethyl ester on treating them with concentrated ammonia.

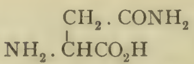
Asparaginimide,  $\begin{array}{l} NH_2 . CH . CO \\ \quad CH_2 . CO \end{array} > NH$ (?), consists of needles, which char at about 250°. It is produced when ammonia (B. **21**, R. 87) acts upon bromsuccinic ester.

Phenylaspartic Acid, $C_6H_5NH . CH(CO_2H)CH_2 . CO_2H$, melting at 131°, is formed from the action of bromsuccinic acid upon aniline. *Phenylasparaginanil*, $C_6H_5NHC_2H_3C_2O_2 . NC_6H_5$, melts at 210°. It results on adding aniline to maleïnanil (A. **239**, 137).

l-Aspartic Acid,  $\begin{array}{l} CH(NH_2) . CO_2H \\ CH_2 . CO_2H \end{array}$, occurs in the vinasse obtained from the beet root, and is procured from albuminous bodies in various reactions. It is prepared by boiling asparagine with alkalies and acids (B. **17**, 2929).

Naturally occurring aspartic acid is lævo-rotatory; it crystallizes in rhombic prisms or leaflets, and dissolves with difficulty in water. Nitrous acid converts it into ordinary l-malic acid (B. **28**, 2769).

d-*Aspartic Acid* is produced when d-asparagine is boiled with dilute hydrochloric acid (B. **19**, 1694).

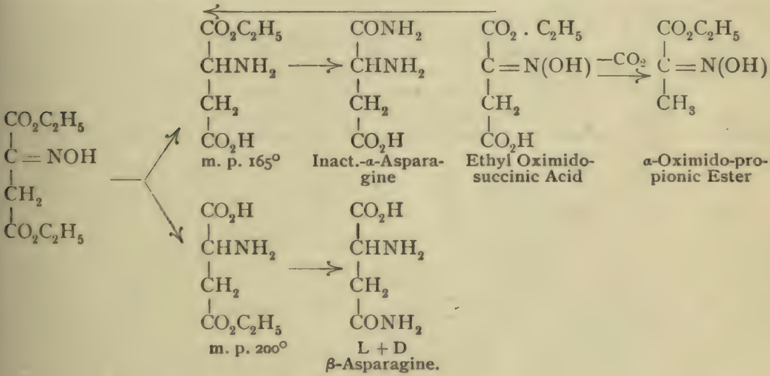
l- and d-Asparagine,  $\begin{array}{l} \quad CH_2 . CONH_2 \\ NH_2 . CHCO_2H \end{array}$ + H_2O, are the monamides of the two optically active aspartic acids, and are isomeric with malamide.

Historical.—As early as 1805 Vauquelin and Robiquet discovered the lævo-asparagine in asparagus. Liebig, in 1833, established its true composition. Kolbe (1862) was the first to regard it as the amide of amidosuccinic acid. Piutti (1886) discovered dextro-asparagine in the sprouts of vetches, in which it occurs together with much lævo-asparagine.

Lævo-asparagine is found in many plants, chiefly in their seeds; in asparagus (*Asparagus officinalis*), in beet-root, in peas, in beans, and in vetch sprouts, from which it is obtained on a large scale, and also in wheat. The lævo- and dextro-asparagines not only occur together in the sprouts of vetches, but they are found together if asparaginimide, produced from bromsuccinic ester, is heated to 100° with ammonia, or by the action of alcoholic ammonia upon β-aspartic ester (B. **20**, R. 510; B. **22**, R. 243). Dextro-asparagine, from the sprouts of vetches, has been produced on heating maleïc anhydride to 110° with alcoholic ammonia (B. **29**, 2070).

Both optically active asparagines crystallize in rhombic, right and left hemihedral crystals, which dissolve slowly in hot water, in alcohol and ether, but they are not easily soluble. It is not possible for them to combine in aqueous solution to an optically inactive asparagine. It is remarkable that the dextro-asparagine has a sweet taste, while the lævo-form possesses a disagreeable and cooling taste. Pasteur assumes that the nerve substance dealing with taste behaves toward the two asparagines like an optically active body, and hence reacts differently with each.

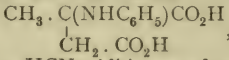
Constitution of the Asparagines.—When the oxime of oxalacetic ester is reduced with sodium amalgam, either α- or β-ethyl-amido-succinic acid is formed with a partial saponification, depending upon the conditions of the reaction. The constitution of the α-acid, melting at 165°, follows from its formation by the reduction of the two probable, spacial isomeric oximidosuccinic ethyl ester acids, which split off CO_2 and yield α-oximidopropionic acid (p. 371). Hence, it may be inferred that the acid melting with decomposition at 200° contains the amido group in the β-position with reference to the carboxethyl group (B. **22**, R. 241). Ammonia converts both acids into their corresponding amido-acids. We obtain inactive α-asparagine from the α-acid, and from the β-acid a mixture of the two optically active β-asparagines results:

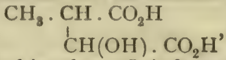


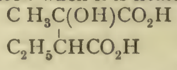
Isoasparagine, $\begin{array}{l} CH_2 . CO_2H \\ | \\ NH_2CH . CONH_2 \end{array}$, results from the action of aluminium amalgam upon potassium amidofumaramidate (C. 1897, I, 364).

Malic Acid Homologues are formed: by the addition of hydrocyanic acid to β-ketonic esters; by the addition of ClOH to alkylic maleïc acids and subsequent reduction; and by the reduction of alkylic oxalacetic esters.

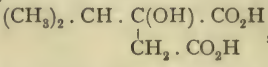
α-Oxypyrotartaric Acid, Citramalic Acid, α-Methyl Malic Acid, $\begin{array}{l} CH_3C(OH)CO_2H \\ \quad | \\ \quad CH_2 . CO_2H \end{array}$, melting at 119°, is produced (1) in the oxidation of isovaleric acid (p. 248) with nitric acid; (2) from acetoacetic ester by means of CNH and HCl, and (3) by the reduction of chlorcitramalic acid, the addition product resulting from the union of ClOH to citraconic acid. It breaks down at about 200° into water and citraconic anhydride (B. **25**, 196). *β-Amidopyrotartaric Acid*, [d + l] homoaspartic acid, $\begin{array}{l} CH_3 . C(NH_2)CO_2H \\ \quad | \\ \quad CH_2CO_2H \end{array}$ + H_2O, melts when anhydrous at 166°. Its diamide results from the action of ammonia upon ita-, citra-, and mesaconic esters (B. **27**, R. **121**). When it crystallizes it splits into the d- and l-acids.

β-Anilidopyrotartaric Acid,  $\begin{array}{l}CH_3 . C(NHC_6H_5)CO_2H \\ \vert \\ CH_2 . CO_2H\end{array}$, melting at 135°, results from the rearrangement of the HCN-addition product of acetoacetic ester with aniline, and the subsequent saponification with caustic potash. When heated, it passes into β-anilidopyrotartranil and citraconanil (A. **261**, 138).

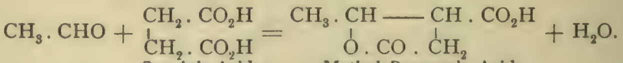
β-Methyl Malic Acid,  $\begin{array}{l}CH_3 . CH . CO_2H \\ \vert \\ CH(OH) . CO_2H\end{array}$, is a colorless syrup, readily soluble in water, in alcohol, and in ether. It is formed when methyl oxalacetic ester is reduced with sodium amalgam, and in an active l- form from a citraconic acid solution by the action of a fungus (B. **27**, R. 470). Mesaconic acid and citraconic anhydride (B. **25**, 196, **1484**) are produced when it is heated.

α,β-Methyl Ethyl Malic Acid,  $\begin{array}{l}CH_3C(OH)CO_2H \\ \vert \\ C_2H_5CHCO_2H\end{array}$, melts at 131.5–132° (B. **26**, R. **190**).

Trimethyl Malic Acid melts at 155° (10 sec. 1°), and is obtained from dimethyl acetoacetic ester with prussic acid, with subsequent saponification by hydrochloric acid (B. **29**, 1543, 1619).

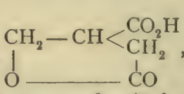
Isopropyl Malic Acid,  $\begin{array}{l}(CH_3)_2 . CH . C(OH) . CO_2H \\ \qquad\qquad\quad \vert \\ \qquad\qquad\quad CH_2 . CO_2H\end{array}$, from brom-pimelic ester (A. **267**, 132), melts at 154°.

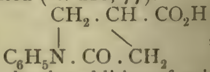
Paraconic Acids are γ-lactonic acids. Like the γ-oxyalkylic malonic acids, they are converted by alkalies and alkaline earths into salts of the corresponding oxysuccinic acids. When the latter are set free from their salts they immediately break down into water and lactonic acids. The alkylic paraconic acids are formed when sodium succinate or pyrotartrate and aldehydes (acetaldehyde, chloral, propionic aldehyde) are condensed by means of acetic anhydride at 100–120° (Fittig, A. **255**, 1):

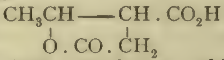


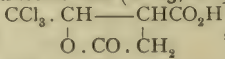
$$CH_3 . CHO + \begin{array}{l}CH_2 . CO_2H \\ \vert \\ CH_2 . CO_2H\end{array} = \begin{array}{l}CH_3 . CH — CH . CO_2H \\ \quad\ \vert \qquad\qquad \vert \\ \quad\ O . CO . CH_2\end{array} + H_2O.$$

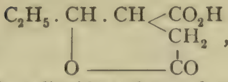
Succinic Acid Methyl Paraconic Acid.

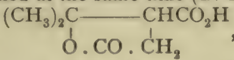
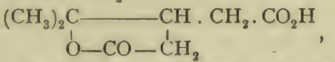
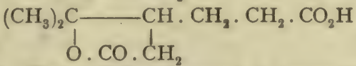
Paraconic Acid,  $\begin{array}{l}CH_2 — CH\begin{cases}CO_2H \\ CH_2\end{cases} \\ \vert \qquad\qquad\quad \vert \\ O ——————— CO\end{array}$, is best prepared by boiling itabrompyrotartaric acid with water and acidulating the calcium salt of the corresponding oxysuccinic acid—*itamalic acid*, formed on boiling itachlorpyrotartaric acid with a soda solution. It melts at 57–58°. When boiled with bases, it forms salts of itamalic acid; it yields citraconic anhydride when it is distilled (A. **216**, 77).

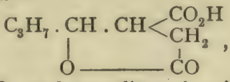
Pseudoitaconanilic Acid, γ-anilidopyrotartro-lactamic acid,  $\begin{array}{l}\quad\ \ CH_2 . CH . CO_2H \\ \quad\ \ \vert \qquad \diagdown \\ C_6H_5N . CO . CH_2\end{array}$, melting at 190°, is formed from itaconic acid (A. **254**, 129), by the addition of aniline, and the lactam formation.

Methyl Paraconic Acid,  $\begin{array}{l}CH_3CH — CH . CO_2H \\ \quad\ \vert \qquad\quad \vert \\ \quad\ O . CO . CH_2\end{array}$, melts at 84.5°. When distilled, methyl paraconic acid yields valerolactone, ethidene propionic acid (p. 283), methylitaconic acid, and methyl citraconic acid (B. **23**, R. **91**).

Trichlormethyl Paraconic Acid,  $\begin{array}{l}CCl_3 . CH — CHCO_2H \\ \qquad\ \vert \qquad\quad \vert \\ \qquad\ O . CO . CH_2\end{array}$, melting at 97°, is changed by cold baryta water into isocitric acid (see this).

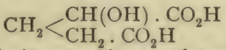
Ethyl Paraconic Acid,  , melts at 85° C. When distilled, it breaks up chiefly into carbon dioxide and caprolactone (p. 346). Isomeric hydrosorbic acid is formed at the same time (B. **23**, R. 93).

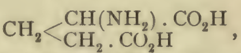
Terebic Acid,  , *Terpenylic Acid,*  , and *Homoterpenylic Acid,*  , are three oxidation products of turpentine oil. They will be discussed in connection with pinene, the principal ingredient of the oil.

Propylparaconic Acid,  , melts at 73.5°. γ-Heptolactone, heptylenic acid, $C_7H_{12}O_2$, and propylitaconic acid, $C_8H_{12}O_4$ (B. **20**, 3180), are produced by the distillation of propylparaconic acid.

Isopropylparaconic Acid melts at 69°, and when distilled decomposes into γ-isoheptolactone and isoheptylenic acid.

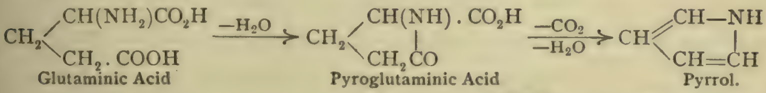
OXYGLUTARIC ACID GROUP.

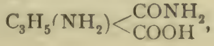
α-**Oxyglutaric Acid,**  $CH_2<\begin{matrix}CH(OH).CO_2H\\CH_2.CO_2H\end{matrix}$ (A. **208**, 66, and B. **15**, 1157), is obtained by the action of nitrous acid upon glutaminic acid; it occurs in molasses. It crystallizes with difficulty, and melts at 72°. Heated with hydriodic acid, it yields glutaric acid (p. 452). When heated, it readily passes into its *lactone*, melting at 49–50° (A. **260**, 129).

Glutaminic Acid, *α*-Amidoglutaric Acid,  $CH_2<\begin{matrix}CH(NH_2).CO_2H\\CH_2.CO_2H\end{matrix}$, contains an asymmetric carbon atom (p. 45), and therefore it can, like malic acid (p. 487), appear in three modifications. Dextro- or ordinary glutaminic acid occurs in various seeds and in the sprouts of vetches, as well as with aspartic acid in the molasses from beet root, and is formed along with other compounds (p. 351) when albuminoid substances are boiled with dilute sulphuric acid. It consists of brilliant rhombohedra, soluble in hot water but insoluble in alcohol and ether. It melts at 202–202.5°, and suffers partial decomposition.

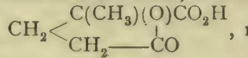
l-Glutaminic acid is obtained from the inactive variety by means of *Penicillium glaucum* (p. 68).

Inactive [d + l] glutaminic acid results from ordinary glutaminic acid on heating it to 150–160° with baryta water, and from *α*-isonitrosoglutaric acid (A. **260**, 119). It melts at 198°, and by repeated crystallization breaks down into d- and l-glutaminic acid crystals (B. **27**, R. 269, 402; **29**, 1700). [d + l] **Pyroglutaminic Acid,** melting at 182–183°, is the γ-lactam of the glutaminic acid, which results on heating ordinary glutaminic acid to 190°, and on continued heating breaks down into CO_2 and pyrrol (B. **15**, 1342):



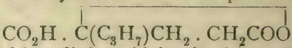
Glutamine, *α*-amidoglutaramic acid,  $C_3H_5(NH_2)<\begin{matrix}CONH_2\\COOH\end{matrix}$, occurs together with asparagine in beet-root, in sprouts and other plants (B. **29**, 1882, C. 1897, I, 105). It is optically inactive.

γ-**Carbovalerolactonic Acid**, α-methylglutolactonic acid, valerolactone-γ-carboxylic acid,



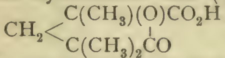
$CH_2<\begin{array}{l}C(CH_3)(O)CO_2H\\ \quad\quad\quad\quad\ |\\ CH_2—CO\end{array}$

, melting from 68–70°, is deliquescent, and is produced (1) by oxidizing γ-isocaprolactone (p. 346) with nitric acid (A. **208**, 62); and (2) by the action of potassium cyanide and hydrochloric acid upon lævulinic acid (p. 379). *Isopropylglutolactonic Acid*,



$CO_2H\,.\,\overline{C(C_3H_7)CH_2\,.\,CH_2COO}$

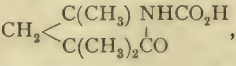
, melting at 67°, has been obtained from δ-dimethyl lævulinic acid by the interaction of prussic acid and hydrochloric acid (A. **288**, 185). *α-Oxy-a_1a_1a-trimethylglutolactonic Acid*,



$CH_2<\begin{array}{l}C(CH_3)(O)CO_2H\\ \quad\quad\quad\quad\ |\\ C(CH_3)_2CO\end{array}$

, melting at 103°, is formed from brom-trimethyl glutaric acid on boiling it with caustic potash, as well as from mesitonic acid, prussic acid, and hydrochloric acid (A. **292**, 220).

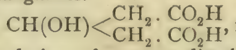
Mesitylic Acid, a-Amido-aa_1a_1-trimethyl glutaric lactam,



$$CH_2<\begin{array}{l}C(CH_3)\ NHCO_2H\\ \quad\quad\quad\quad\ |\\ C(CH_3)_2CO\end{array},$$

melts at 174°, when anhydrous, and is obtained by boiling the hydrochloric acid addition-product arising from mesityl oxide, cyanide of potassium, and alcohol (see mesitonic acid (p. 381). It is converted into unsym. dimethyl succinimide (B. **14**, 1074) by potassium permanganate.

β-**Oxyglutaric Acid**,



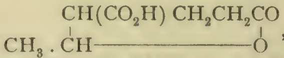
$CH(OH)<\begin{array}{l}CH_2\,.\,CO_2H\\ CH_2\,.\,CO_2H\end{array}$

, melting at 95°, has been prepared by reducing an aqueous solution of acetone dicarboxylic acid (B. **24**, 3250). Sulphuric acid converts it into glutaconic acid (p. 467). The *diethyl ester* boils at 150° (11 mm.) (B. **25**, 1976). Ammonia changes the ester to the diamide, which passes over into glutaconimide when treated with sulphuric acid.

β-**Chlorglutaric Acid** results on treating glutaconic acid with hydrochloric acid. From it and glutaconic acid there results, by the action of ammonia:

β-Amidoglutaric Acid, $CO_2H\,.\,CH_2\,.\,CH(NH_2)CH_2\,.\,CO_2H$, melting at 247–248° with decomposition.

δ-**Caprolactone-γ-Carboxylic Acid**,



$\begin{array}{l}\quad\quad\ \ CH(CO_2H)\ CH_2CH_2CO\\ \quad\quad\quad\ |\quad\quad\quad\quad\quad\quad\quad\quad\quad |\\ CH_3\,.\,CH—————O\end{array}$

, melting at 107°, is produced in the reduction of a-acetglutaric acid (B. **29**, 2368). Compare also p. 278 and $\gamma\delta$-hexenic acid (p. 284).

a-**Hydroxyadipic Acid**, see B. **28**, R. 466.

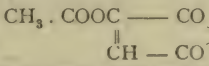
a-Hydroxysebacic Acid, see B. **27**, 1217.

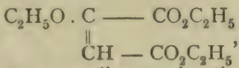
B. OXY-OLEFINE DICARBOXYLIC ACIDS.

Oxymethylene Malonic Ester, $(CO_2C_2H_5)_2C = CHOH$, boiling at 218°, forms a gray copper salt, melting at 138°. **Ethoxymethylene Malonic Ester**, $(CO_2C_2H_5)_2C = CHOC_2H_5$, boiling at 280°, is obtained from malonic ester and orthoformic ester. It combines readily with malonic ester, forming dicarboxylic glutaconic ester or methenylbismalonic ester, $(CO_2C_2H_5)_2C = CH\,.\,CH(CO_2C_2H_5)_2$ (B. **26**, 2731, and private communication from L. Claisen).

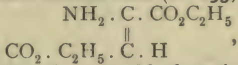
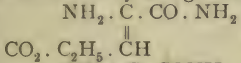
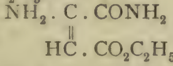
Cyclic oxymethylene malonic acid derivatives are produced by the action of amidines, hydrazine, and hydroxylamine upon dicarboxyl glutaconic ester (B. **27**, 1658; **30**, 821, 1083).

Amidomethylene Malonic Ester, $(CO_2C_2H_5)_2C = CHNH_2$, melting at 67°, can be obtained from ethoxymethylene malonic ester and dicarboxyl-glutaconic ester by the action of ammonia (Chem. Soc. **59**, 746).

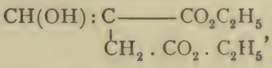
Acetoxymaleïc Anhydride,  $\begin{matrix}CH_3 . COOC - CO \\ \| \\ CH - CO\end{matrix}{>}O$, melting at 90°, is produced by acting on acetylene dicarboxylic acid and oxalacetic acid with acetic anhydride at 100°. Alcohol converts it into a mixture of acetic and oxalacetic esters (B. **28**, 2511).

Ethoxyfumaric Ester,  $\begin{matrix}C_2H_5O . C - CO_2C_2H_5 \\ \| \\ CH - CO_2C_2H_5\end{matrix}$, boiling at 130° (11 mm.), is produced when ethyl iodide acts upon silver oxalacetic ester, as well as from ordinary dibromsuccinic ester and sodium ethylate. Diethoxysuccinic ester is produced simultaneously. It is the sodium salt of this body that is formed through the action of sodium ethylate upon the ethoxyfumaric ester (B. **28**, 2512). Cold dilute alkalies change the ester to *ethoxyfumaric acid*, melting at 133°. Acetic anhydride converts this into liquid **ethoxymaleïc anhydride. Ethoxymaleïc Acid**, produced by the action of water on the anhydride, melts at 126°. Hydrochloric acid changes ethoxyfumaric and ethoxymaleïc esters into oxalacetic acid (B. **29**, 1792).

Probably the ammonia addition-product of oxalacetic ester is an ammonium derivative of ethoxyfumaric ester, $CO_2C_2H_5 . C(ONH_4) . CHCO_2C_2H_5$. It melts at 83°, and gradually changes to oxalcitric acid lactone ester (A. **295**, 346).

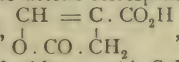
Ethyl Amidofumaric Ester,  $\begin{matrix}NH_2 . C . CO_2C_2H_5 \\ \| \\ CO_2 . C_2H_5 . C . H\end{matrix}$, boiling at 142° (20 mm.), is obtained by the action of ammonia upon chlorfumaric ethyl ester and chlormaleïc ethyl ester; also by the rapid distillation of oxalacetic ester (A. **295**, 344). Copper acetate slowly changes it to oxalacetic ester. **Ethyl Amidofumaramide Ester,**  $\begin{matrix}NH_2 . C . CO . NH_2 \\ \| \\ CO_2 . C_2H_5 . CH\end{matrix}$ (?), melts at 139°, and **Ethyl Amidomaleïnamide Ester,**  $\begin{matrix}NH_2 . C . CONH_2 \\ \| \\ HC . CO_2C_2H_5\end{matrix}$ (?), melts at 119°. See isoasparagine, p. 491 (C. 1897, I, 364).

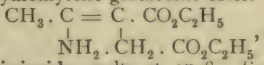
Oxymethylene Succinic Ester, Formyl Succinic Ester,

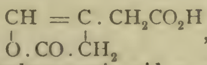


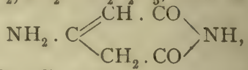
$$\begin{matrix}CH(OH) : C - CO_2C_2H_5 \\ | \\ CH_2 . CO_2 . C_2H_5\end{matrix},$$

boiling at 125° (16 mm.), results from the condensation of succinic ester with formic ester and sodium ethylate. Ferric chloride imparts a violet color to it (B. **26**, R. 91). It can be reduced to itamalic ester (p. 492), and the alkalies decompose it into alcohol, formic acid, and succinic acid (B. **27**, 3186). See B. **26**, 2061, for the action of hydrazine. The lactone corresponding to oxymethylene succinic acid is probably:

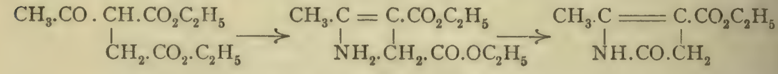
Aconic Acid,  $\begin{matrix}CH = C . CO_2H \\ | \quad\quad\quad | \\ O . CO . CH_2\end{matrix}$, melting at 164°, which results on boiling itadibromtartaric acid with water (A. Spl. 1, 347; B. **27**, 3440). The *methyl ester* melts at 84°. Aconic acid bears the same relation to ethoxymethylene succinic ester that coumalic acid sustains to methyl methoxymethylene glutaconic ester.

α-**Aminoethidene Succinic Ester,**  $\begin{matrix}CH_3 . C = C . CO_2C_2H_5 \\ | \quad\quad | \\ NH_2 . CH_2 . CO_2C_2H_5\end{matrix}$, melts at 72° (B. **20**, 3058) and *α*-**Aminoethidene Succinimide** melts at 274°. See acetosuccinic ester.

Mucolactonic Acid,  $\begin{matrix}CH = C . CH_2CO_2H \\ | \quad\quad | \\ O . CO . CH_2\end{matrix}$, is obtained by heating dibromadipic acid, $C_6H_8Br_2O_4$ (from hydromuconic acid, p. 467), with silver oxide. It melts at 122–125°.

β-Amidoglutaconic Ester, $CO_2C_2H_5 . CH = C(NH_2)CH_2 . CO_2C_2H_5$, boils at 157–158° (12 mm.). **Glutazine,** β-amidoglutaconimide,  $NH_2 . C\left\langle\begin{array}{l} CH . CO \\ CH_2 . CO \end{array}\right\rangle NH$, melts with decomposition at 300° (compare acetone dicarboxylic ester).

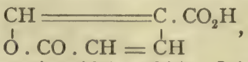
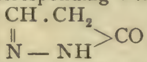
Lactams of γ-amido unsaturated dicarboxylic acids result when ammonia and primary amines act upon acetoacetic ester (A. **260**, 137):



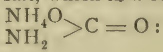
$$\begin{array}{l} CH_3.CO . CH.CO_2C_2H_5 \\ \quad | \\ \quad CH_2.CO_2.C_2H_5 \end{array} \longrightarrow \begin{array}{l} CH_3.C = C.CO_2C_2H_5 \\ \qquad | \qquad | \\ \quad NH_2.CH_2.CO.OC_2H_5 \end{array} \longrightarrow \begin{array}{l} CH_3.C = C.CO_2C_2H_5 \\ \qquad | \qquad\quad | \\ \quad NH.CO.CH_2 \end{array}$$

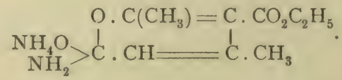
Lactams of δ-amido unsaturated dicarboxylic acids are formed when ammonia and primary amines act upon α-acetylglutaric ester (B. **24**, R. 661).

C. OXYDIOLEFINE DICARBOXYLIC ACID.

Coumalic Acid,  $\begin{array}{l} CH = C . CO_2H \\ | \qquad\qquad\qquad | \\ O . CO . CH = CH \end{array}$, melts with decomposition at 206°. It is isomeric with comanic acid (see this). It is produced when malic acid is heated with concentrated sulphuric acid or $ZnCl_2$. Oxymethylene acetic acid, $HO . CH = CH . CO_2H$ (p. 361), is an intermediate product. Its condensation gives rise to the coumalic acid, since the latter is also formed when sulphuric acid acts upon oxymethylene acetic ester (A. **264**, 269). Like chelidonic and meconic acids, it forms yellow-colored salts with the alkalies. Coumalic acid is decomposed by boiling baryta water into glutaconic acid (p. 467) and formic acid. Boiling dilute sulphuric acid breaks it down into CO_2 and crotonaldehyde (p. 208). Ammonia converts it into the corresponding *δ-lactam*, the so-called *β-oxynicotinic acid.* It combines to pyrazolon,  $\begin{array}{l} CH . CH_2 \\ \| \\ N - NH \end{array}\!\!>CO$ (p. 367) (B. **27**, 791), with a dilute hydrazine solution.

Oxymethylene Glutaconic Acid, $HO . CH = C(CO_2H) . CH = CH . CO_2H$. Coumalic acid might be regarded as the δ-lactone of this oxy-acid. It is not known in a free state, but *methoxymethylene glutaconic methyl ester*, $CH_3O . CH = C(CO_2CH_3) . CH = CH . CO_2CH_3$, melting at 62°, is produced on treating coumalic acid with methyl alcohol and hydrochloric acid (A. **273**, 164).

Isodehydracetic Acid, Dimethyl Coumalic Acid,  $\begin{array}{l} C(CH_3) = C.CO_2H \\ | \qquad\qquad\qquad | \\ O . COCH = C.CH_3 \end{array}$, melting at 155°, is isomeric with dehydracetic acid (see this). It is produced (1) by the action of concentrated sulphuric acid upon acetoacetic ester; (2) from β-chlorisocrotonic ester and sodium acetoacetic ester (A. **259**, 179). It decomposes when heated to 200–205° into CO_2 and *mesitene lactone.* The *methyl ester* melts at 67–67.5° and boils at 167° (14 mm.). The *ethyl ester* boils at 166° (12 mm.). The latter takes up ammonia and yields an ammonium salt, which in a certain respect is similarly constituted to ammonium carbamate,  $\begin{array}{l} NH_4O \\ NH_2 \end{array}\!\!>C = O$:



$$\begin{array}{l} \qquad\qquad O . C(CH_3) = C . CO_2C_2H_5 \\ \qquad\qquad | \qquad\qquad\qquad | \\ \begin{array}{l} NH_4O \\ NH_2 \end{array}\!\!>C . CH = C . CH_3 \end{array}$$

β-Oxynicotinic Acid and β-oxy-dimethyl nicotinic acid are δ-lactams corresponding to coumalic and isodehydracetic acids. The ethyl ester of the second lactam—the so-called **carboxethyl pseudolutidostyril,** melting at 137°—results from the action of ammonia upon ethyl isodehydracetic ester at 100–140°. The same δ-lactam is obtained in the condensation of β-amidocrotonic ester (p. 363) (A. **259**, 172).

13. KETONE DICARBOXYLIC ACIDS.

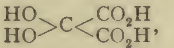
Dibasic carboxylic acids, containing a ketone group in addition to the carboxyl groups, are mainly synthesized as follows:

1. By the introduction of acid radicals into malonic esters.
2. By introducing the residues of acid esters into acetoacetic ester.
3. By the condensation of oxalic esters with fatty acid esters.

These methods of formation will be more fully considered under the individual groups of the monoketone carboxylic acids. The position of the two carboxyl groups is again the basis for their classification as the *ketomalonic acid group*, the *ketosuccinic acid group*, the *ketoglutaric acid group*, etc.

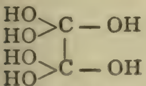
KETOMALONIC ACID GROUP.

Mesoxalic Acid, *Dioxymalonic Acid*, [*Propandiol-diacid*],

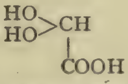


$$\begin{matrix}HO\\HO\end{matrix}>C<\begin{matrix}CO_2H\\CO_2H\end{matrix},$$

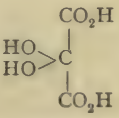
melts at 115° without loss of water. It is assumed that in this acid as in glyoxylic acid, and oxalic acid crystallized from water, the water molecule is not present as water of crystallization, but that the double union between the carbon and oxygen has been severed, and that it has attached itself to the CO-group, hence two hydroxyl groups are produced, whence the name dioxymalonic acid:



Ortho-oxalic Acid



Glyoxylic Acid



Mesoxalic Acid.

Furthermore, esters of mesoxalic acid derived from both forms are known. They are the *oxo-* and the *dioxymalonic acid esters*. Mesoxalic acid is formed from amidomalonic acid by oxidation with iodine in an aqueous solution of potassium iodide; from dibrom-malonic acid by boiling with baryta water or silver oxide; by boiling alloxan (mesoxalyl urea) with baryta water; and by oxidizing glycerol with nitric acid, nitre, and bismuth subnitrate (B. **27**, R. 666).

Mesoxalic acid crystallizes in deliquescent prisms. At higher temperatures it decomposes into CO_2 and glyoxylic acid, $CHO . CO_2H$. It breaks up into CO and oxalic acid by the evaporation of its aqueous solution.

Mesoxalic acid deports itself like a ketonic acid, inasmuch as it unites with primary alkaline sulphites, and when acted upon by sodium amalgam in aqueous solution, it is changed to tartronic acid. It combines with hydroxylamine and phenylhydrazine.

Salts.—Barium mesoxalate, $C(OH)_2<\genfrac{}{}{0pt}{}{CO_2}{CO_2}>Ba$, and *calcium mesoxalate*, are crystalline powders, not very soluble in water. The *ammonium salt*, $C(OH)_2 . (CO_2 . NH_4)_2$, crystallizes in needles. The *silver salt*, $C(OH)_2 . (CO_2Ag)_2$, when boiled with water affords mesoxalic acid, silver oxalate, silver, and CO_2. See B. **27**, R. 667, for the *bismuth salt*.

Esters.—Two series of esters may be derived from mesoxalic acid —the anhydrous or **oxomalonic esters,** $CO(CO_2R')_2$, and the **dioxymalonic esters,** $C(OH)_2(CO_2R')_2$. The first are produced when the reaction-product from bromine and acetotartronic ester is distilled, and also in the distillation of dioxymalonic ester under diminished pressure. The oxomalonic esters absorb water with avidity, and thereby change to their corresponding dioxymalonic esters. The two compounds bear the same relation to each other that chloral sustains to chloral hydrate:

$$CCl_3 . CHO \text{ Chloral } \xrightarrow{H_2O} CCl_3 . CH(OH)_2 \text{ Chloral Hydrate}$$

$$CO(CO_2C_2H_5) \text{ Oxomalonic Ester} \xrightarrow{H_2O} C(OH)_2(CO_2C_2H_5)_2 \text{ Dioxymalonic Ester.}$$

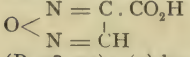
Oxomalonic Ethyl Ester, $CO(CO_2C_2H_5)_2$, boiling at 100–101° (14 mm.), sp. gr. 1.1358 (16°), possesses a bright greenish-yellow color. It is a mobile liquid, with a faint but not disagreeable odor. When heated under ordinary pressure it breaks down partly into CO and oxalic ester (B. **27**, 1305). **Dioxymalonic Ethyl Ester,** $C(OH)_2 . (CO_2C_2H_5)$, melting at 57°, dissolves easily in water, alcohol, and ether. **Diethoxymalonic Ester,** $(C_2H_5O)_2C(CO_2C_2H_5)$, melts at 43° and boils at 228° (B. **30**, 490). **Diacetdioxymalonic Ester,** $(CH_3CO . O)_2C(CO_2C_2H_5)_2$, melts at 145°.

Nitrogen Derivatives of Mesoxalic Acid.

Isonitrosomalonic Acid, $C(N . OH)(CO_2H)_2$, is formed by the action of hydroxylamine (B. **16**, 608, 1621) upon violuric acid (see this) and mesoxalic acid, also from its *ethyl ester*, produced when nitrous acid is conducted into the solution of sodium malonic ester. It melts at 126°, decomposing at the same time into hydrocyanic acid, carbon dioxide, and water. *Dimethyloximidomesoxalamide*, $N(OH) : C(CONHCH_3)_2$, melts at 228° (B. **28**, R. 912).

Phenylhydrazidomesoxalic Acid, $C_6H_5NH . N : C(CO_2H)_2$, melts with decomposition at 163°. It is obtained (1) from mesoxalic acid and phenylhydrazine; (2) by the saponification of its ethyl ester. **Ethyl Phenylhydrazidomesoxalic Acid,** $C_6H_5NH . N = C<\genfrac{}{}{0pt}{}{CO_2C_2H_5}{CO_2C_2H_5}$, melts at 115°. **Phenylhydrazidomesoxalic Ethyl Ester,** $C_6H_5NH . N = C(CO_2C_2H_5)_2$, is obtained both from mesoxalic ester and phenylhydrazine, as well as from sodium malonic ester and diazobenzene chloride (B. **24**, 866, 1241; **25**, 3183). **Hydrazidomesoxalamide,** $NH_2 . N : C(CONH_2)_2$, melting at 175°, results from dibrom-malonamide and hydrazine (B. **28**, R. 1052).

Cyanoximido-acetic Acid, $CN . C : N(OH)CO_2H$, melts, when anhydrous, at 129° with much foaming. It is produced (1) from isomeric *furazan carboxylic acid*,



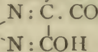
(p. 483); (2) on boiling furazan dicarboxylic acid with water (B. **28**, 72); (3) by the action of hydroxylamine hydrochloride upon dioxytartaric acid (see this) in acid solution, β-dioximidosuccinic acid (B. **24**, 1988) being formed at the same time; (4) when nitrous acid acts upon oxazolonhydroxamic acid (B. **28**, 761).

Cyanoximido-acetic Ester, $CN . C : N(OH) . CO_2C_2H_5$, from sodium cyanacetic ester (p. 440) and amyl nitrile (B. **24**, R. 595), melts at 127–128°. *Desoxyfulminuric Acid*, cyanisonitroso acetamide, CN . C : N(OH) . C(OH) : NH (see p. 238). *Cyanisonitroso-acethydroxamic Acid*, CN . C : (NOH) . C(OH) : N . OH, melting at 107°, is formed from formyl chloridoxime (p. 233) and ammonia.

Benzene azocyanacetic Ester, $C_6H_5NH . N : C(CN)CO_2C_2H_5$, melting at 125°, is formed from cyanacetic ester and diazobenzene chloride (B. **27**, R. 393). Consult B. **28**, R. 997 for substitution derivatives of this body.

Phenylhydrazone-mesoxalonitrile, $(CN)_2C = N . NHC_6H_5$, melts with decomposition between 130° and 144°. It is formed when diazobenzene nitrate acts upon potassium malononitrile (B. **29**, 1174).

Oxazomalonic Acid results from the action of nitric oxide and sodium ethylate upon malonic ether. Caustic soda converts the unstable reaction product into the *sodium salt*, $Na_2O : C(CO_2Na)_2 + 2H_2O$. This as well as the other salts explode very easily, particularly when they are anhydrous (B. **28**, 1795).

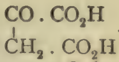
Oxyfurazan Carboxylic Acid,  $O\!<\!\begin{matrix} N : C . CO_2H \\ | \\ N : COH \end{matrix}$, see oxyfurazan acetic acid (p. 500). Mesoxalamide derivatives have been obtained by the addition of $COCl_2$ to phenyl- and toluylisocyanides. Thus, phenylisocyanide gave:

Mesoxanilide-diimide Chloride, $CO[CCl = NC_6H_5]_2$, melting at 145–152° (15–20 mm.) (A. **270**, 286). *Diamidomalonamide*, diamidomesoxalamide, $CO_2NH_2C(NH_2)CONH_2$, consists of white crystals, decomposing at 150°. It results from the action of alcoholic ammonia upon dibrom-malonic ester (p. 440), and upon the loss of ammonia passes into *imidomalonamide*, $CONH_2 . C : NH . CONH_2$ (B. **24**, 3002).

Acetyl Malonic Acid, $CH_3 . CO . CH(CO_2H)_2$. Its ethyl ester results from the interaction of chlorcarbonic ester and sodium acetoacetic ester (p. 388) (B. **22**, 2617; **21**, 3567). It is a mobile liquid, boiling at 120° (17 mm.). When saponified by the alkalies it decomposes into CO_2, acetone, and acetic acid.

Acetyl Cyanacetic Acid, $CH_3 . CO . CH(CN)CO_2C_2H_5$, melting at 26° and boiling at 119° (15–20 mm.), is produced when acetyl chloride acts upon sodium cyanacetic ester. *Propionyl Cyanacetic Ester* boils at 155–165° (50 mm.) (B. **21**, R. 187, 354; **22**, R. 407).

KETOSUCCINIC ACID GROUP.

Oxalacetic Ester, *Oxosuccinic Ester* [*Butanon-diacid*],  $\begin{matrix} CO . CO_2H \\ | \\ CH_2 . CO_2H \end{matrix}$. The free acid is not stable. Its *ethyl ester*, boiling at 131–132° (24 mm.), and *methyl ester*, melting at 74–76° and boiling at 137° (39 mm.) (A. **277**, 375), are formed when sodium ethylate (W. Wislicenus) acts upon a mixture of oxalic and acetic esters, and when acetylene dicarboxylic ester is digested with sulphuric acid. When boiled with alkalies it breaks down into alcohol and oxalic and acetic acids (*acid decomposition*). Boiling H_2SO_4 causes it to undergo the ketone decomposition (p. 369) whereby CO_2 and pyroracemic acid ($CH_3 . CO . CO_2H$) are produced. Heated at the ordinary pressure it loses CO and passes into malonic ester (*carbon monoxide decomposition*). Pyroracemic ester is a by-product (B. **28**, 811):

$CO_2C_2H_5 . CO \vdots CH_2 . CO_2C_2H_5$—Acid decomposition,
$CO_2C_2H_5COCH_2 \vdots CO_2C_2H_5$ —Ketone decomposition,
$CO_2 . C_2H_5 \vdots CO \vdots CH_2CO_2C_2H_5$—Carbon monoxide decomposition.

It yields the esters of inactive malic acid by reduction (B. 24, 3416). Ferric chloride imparts a deep red color to the solution of the ester.

It condenses with acetonitrile (B. 25, R. 175) and with acetanilide (B. 24, 1245). Oxalacetic ester and hydroquinone condense under the influence of sulphuric acid to m-oxycoumarine carboxylic ester (B. 28, R. 115).

Oxalacetic ester is both an α- and a β-ketonic ester.

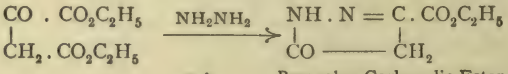
Unsym. **Diethoxysuccinic Ester**, $CO_2C_2H_5\,.\,C(OC_2H_5)_2\,.\,CH_2\,.\,CO_2C_2H_5$, is formed together with ethoxyfumaric ester (p. 495) both from ordinary dibromsuccinic ester and acetone dicarboxylic ester by the action of sodium ethylate. The resulting *diethoxysuccinic acid*, when allowed to stand under greatly reduced pressure or when heated to 100°, loses ether and becomes oxalacetic acid (B. 29, 1792).

Methyl Oxalacetic Ester, $\begin{array}{l}CO\,.\,CO_2C_2H_5\\ \vert\\ CH(CH_3)\,.\,CO_2C_2H_5\end{array}$, is obtained from the esters of oxalic and propionic acids. *Methyl Oxalacetic Anil*, $\begin{array}{r}CO\,.\,CO\\ \vert\qquad\\ CH_3\,.\,CH\,.\,CO\end{array}\!\!>N\,.\,C_6H_5$, melting at 191–192°, is formed from oxalic ester and propionanilide (B. 24, 1256).

Ethyl Oxal-acetic Ester, $CO_2C_2H_5\,.\,CO\,.\,CH(C_2H_5)CO_2C_2H_5$ (B. 20, 3394).

Nitrogen Derivatives of Oxalacetic Acid (B. 24, 1198). Ammonia and oxalacetic ester combine to a body which has one of the following formulas: $CO_2C_2H_5\,.\,C(OH)NH_2\,.\,CH_2\,.\,CO_2C_2H_5$ or $CO_2\,.\,C_2H_5\,.\,C(ONH_4):CH\,.\,CO_2C_2H_5$ (B. 28, 788), see ethoxyfumaric acid, p. 495. *Oximes: β-Oximidosuccinic Ethyl Ester*, melting at 54°, results from the oxime of oxalacetic ester. α-Oximidosuccinic Ethyl Ester Acid, melting at 107°, is produced when water acts upon diisonitrososuccinyl succinic ester. Both bodies, when heated with water, yield CO_2 and α-oximidopropionic acid, $CH_3C:N(OH)CO_2C_2H_5$. Hence, both ester acids are given the structural formula, $CO_2H\,.\,CH_2C:N(OH)CO_2C_2H_5$, and it is assumed that they are stereo-isomerides (B. 24, 1204). *Oximidosuccinic Ester*, $CO_2C_2H_5\,.\,C:N(OH)CH_2\,.\,CO_2C_2H_5$, is a colorless oil (B. 21, R. 351). Compare *aspartic acid* and *asparagine*, pp. 489, 490.

Phenylhydrazine adds itself to oxalacetic ester just the same as ammonia. The addition product, melting at 105°, is either a phenylammonium salt of oxyfumaric acid, or it is a compound similar to aldehyde ammonia. It readily passes into the *phenylhydrazone-oxalacetic ester*, $C_6H_5NH\,.\,N:C<\begin{array}{l}CO_2C_2H_5\\ CH_2\,.\,CO_2C_2H_5\end{array}$, melting at 77°. The reaction products of hydrazine and phenylhydrazine upon oxalacetic ester are the *lactazams* (p. 363) or pyrazolon derivatives (A. 246, 320; B. 25, 3442), *e.g.*:



$$\begin{array}{l}CO\,.\,CO_2C_2H_5\\ \vert\\ CH_2\,.\,CO_2C_2H_5\end{array}\xrightarrow{NH_2NH_2}\begin{array}{l}NH\,.\,N=C\,.\,CO_2C_2H_5\\ \vert\qquad\qquad\quad \vert\\ CO\;\text{——}\;CH_2\end{array}$$

Pyrazolon Carboxylic Ester.

Phenylhydrazone-oxalacetic ester is also formed from acetylene dicarboxylic ester and phenylhydrazine (B. 26, 1721).

Oximido-cyanpyroracemic Ester, $CN\,.\,CH_2\,.\,C=N(OH)CO_2C_2H_5$, melts at 104° (B. 26, R. 375).

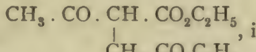
Ammonium Isoxazolonhydroxamate, $\begin{array}{l}\qquad\qquad\;\; N\text{———}O\\ NH_3HO\diagdown\;\;\Vert\qquad\quad\vert\\ HON\diagup C\,.\,C\,.\,CH_2\,.\,CO\end{array}$, decomposes at 156–160°. It is produced in the action of hydroxylamine and ammonia upon oxalacetic ester. See also cyanoximidoacetic acid, p. 498. Alkali changes it to

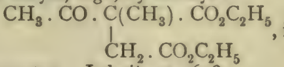
Oxyfurazan-acetic Acid, $O<\begin{array}{l}N:C\,.\,CH_2\,.\,CO_2H\\ \quad\;\;\vert\\ N:COH\end{array}$, consisting of prisms, decomposing at 158°. Potassium permanganate oxidizes it to oxyfurazan carboxylic acid (B. 28, 761).

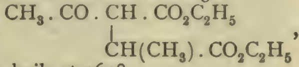
Diazosuccinic Esters are formed when sodium nitrite acts upon the hydrochlorides of aspartic esters. The crude, yellow-colored, easily decomposable esters, when boiled with water, pass into fumaric esters. They revert to aspartic esters on reduction.

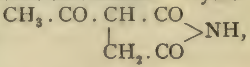
Methyl Diazosuccinamic Ester, $CO_2.CH_3.CN_2.CH_2.CONH_2$, melting at 84°, is formed when ammonia acts upon methyl diazosuccinic ester (B. **19**, 2460; **29**, 763).

Acetosuccinic esters and alkylic acetosuccinic esters are produced when sodium acetoacetic esters and their monoalkylic derivatives are acted upon by esters of the α-monohalogen fatty acids.

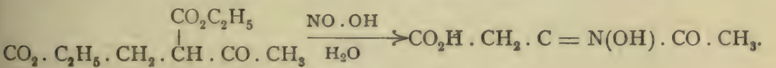
Aceto-succinic Ester,  $\begin{matrix}CH_3.CO.CH.CO_2C_2H_5\\ |\\ CH_2.CO_2C_2H_5\end{matrix}$, is prepared from acetoacetic ester and chloracetic ester. It boils at 254–260°. The hydrogen atom of the CH-group, in the esters, can be replaced by alkyls, *e.g.*, by methyl:

α-**Methyl Aceto-succinic Ester,**  $\begin{matrix}CH_3.CO.C(CH_3).CO_2C_2H_5\\ |\\ CH_2.CO_2C_2H_5\end{matrix}$, is formed from methyl acetoacetic ester and chloracetic ester. It boils at 263°.

β-**Methyl Aceto-succinic Ester,**  $\begin{matrix}CH_3.CO.CH.CO_2C_2H_5\\ |\\ CH(CH_3).CO_2C_2H_5\end{matrix}$, from acetoacetic ester and α-brom-propionic ester, boils at 263°.

By the acid decomposition these esters break down into acetic acid and succinic acid or alkylic succinic acids (pp. 443, 444); by the ketone decomposition the products are CO_2 and γ-ketonic acids (p. 379). Ammonia and primary amines convert the acetosuccinic esters into γ-amidodicarbonic acids, which readily part with alcohol and become γ-lactams (A. **260**, 137). Acetosuccinic ester and ammonia yield: α-amino-ethidene succinic ester (p. 495) and α-amino-ethidene succinimide. Hydrochloric acid converts the latter into *acetosuccinimide*,  $\begin{matrix}CH_3.CO.CH.CO\\ |\\ CH_2.CO\end{matrix}\!\!>\!NH$, melting at 84–87° (C. 1897, I, 283).

Nitrous acid converts acetosuccinic ester, with the alcohol and carbonic acid decompositions, into isonitrosolævulinic acid (compare isonitroso acetone, p. 326):



$$CO_2.C_2H_5.CH_2.\overset{\overset{CO_2C_2H_5}{|}}{C}H.CO.CH_3 \xrightarrow[H_2O]{NO.OH} CO_2H.CH_2.C=N(OH).CO.CH_3.$$

OXO- OR KETOGLUTARIC ACID GROUP.

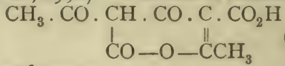
α-**Oxoglutaric Acid** is not known, and the body formerly considered as such is oxymethylene succinic ester (p. 495). *Cyan-oximidobutyric Acid*, $CO_2H.CH_2.CH_2.C=(NOH)CN$, melting at 87°, is a derivative of α-oxoglutaric acid. It is formed when cold sodium hydroxide acts upon *furazan propionic acid* (p. 483). When it is boiled with sodium hydroxide *α-Oximidoglutaric Acid*, $CO_2H.CH_2.CH_2C=N(OH)CO_2H$, melting at 152°, is the product (A. **260**, 106).

Acetone Dicarboxylic Acid, β-keto- or β-oxoglutaric acid, $CO(CH_2CO_2H)_2$, melts at about 130°, and decomposes into CO_2 and acetone. It may be obtained by warming citric acid with concentrated sulphuric acid (v. Pechmann, B. **17**, 2542; **18**, R. 468; A. **278**, 63).

Acetone dicarboxylic acid dissolves readily in water and ether. The same alteration which takes place on heating the acid alone occurs on boiling it with water, acids, or alkalies. The solutions of the acid are colored violet by ferric chloride. Hydrogen reduces the acid to β-oxyglutaric acid (p. 494).

PCl_5 converts the acid into β-chlorglutaconic acid.

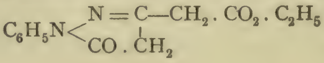
Hydroxylamine changes it to *oximidoacetone dicarboxylic acid*, $CO_2H.CH_2.C(NOH)CH_2CO_2H + H_2O$, melting at 53–54°. In the anhydrous state it melts at 89° (B. **23**, 3762). Nitrous acid converts acetone dicarboxylic acid into diisonitrosoacetone (p. 479) and CO_2 (B. **19**, 2466; **21**, 2998). The acid is condensed by acetic anhydride to *dehydracetcarboxylic acid*,



$$\begin{array}{l}CH_3.CO.CH.CO.C.CO_2H\\ \quad\quad\quad\;\; | \quad\quad\quad\quad\; \| \\ \quad\quad\quad\; CO-O-CCH_3\end{array}$$

(A. **273**, 186). The salts break down into acetone and carbonates.

Esters: Dimethyl Ester boils at 128° (12 mm.). The *diethyl ester* boils at 138° (12 mm.) (B. **23**, 3762; **24**, 4095). The four H-atoms of the two CH_2-groups in it can be successively replaced by alkyls (B. **18**, 2289), and they also readily condense with aldehydes (B. **29**, 994; R. 93). Ammonia and the diethyl ester combine to form β-oxyamidoglutaminic ester, which condenses further to glutazine (see this)—a trioxypyridine derivative (B. **19**, 2694). Alcoholic ammonia produces *β-amidoglutaconic ester* (B. **23**, 3762). Nitrous acid converts the ethyl ester into the oximido-compound, $CO_2C_2H_5C:N(OH)CO.CH_2.CO_2C_2H_5$, which then passes into *oxyisoxazole-dicarboxylic ester*, $CO_2.C_2H_5.C = (NO)C(OH):C.CO_2C_2H_5$ (B. **24**, 857). Fuming nitric acid changes it to the peroxide, $CO_2.C_2H_5.C:N(O)CH_2.C:N(O).CO_2C_2H_5$ (B. **26**, 997). The phenylhydrazones of the acid and of the ester readily change to a corresponding *lactazam*—a *pyrazolon*—derivative,

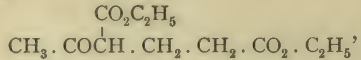


$$C_6H_5N\begin{array}{l}\diagup N = C-CH_2.CO_2.C_2H_5\\ \diagdown CO.\overset{|}{C}H_2\end{array}$$

(B. **24**, 3253).

Acetyl-n-glutaric Acids are produced by the action of β-iodopropionic ester upon the sodium derivatives of acetoacetic ester and alkylic acetoacetic esters:

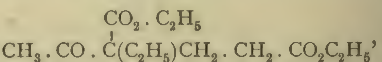
a-Acetglutaric Ester,



$$CH_3.CO\overset{\displaystyle CO_2C_2H_5}{\overset{|}{C}}H.CH_2.CH_2.CO_2.C_2H_5$$

boils at 271–272°.

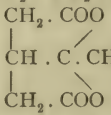
a-Ethyl-a-Acetglutaric Ester,



$$CH_3.CO.\overset{\displaystyle CO_2.C_2H_5}{\overset{|}{C}}(C_2H_5)CH_2.CH_2.CO_2C_2H_5$$

decomposes when it is distilled. By the elimination of carbon dioxide the free acids change into the corresponding δ-ketonic acids (p. 383) (A. **268**, 113).

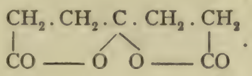
β-Acet-glutaric Acid, $CH_3.CO.CH[CH_2.CO_2H]_2$, melting at 47–50°, is obtained from its *keto-dilactone*,



$$\begin{array}{l}CH_2.COO\\ |\quad\quad\diagup\\ CH.C.CH_3\\ |\quad\quad\diagdown\\ CH_2.COO\end{array}$$

melting at 102° and boiling at 205° (12 mm.), by prolonged boiling with water. The ketodilactone is produced on decomposing β-acettricarballylic ester with boiling hydrochloric acid (A. **295**, 94).

Acetone-diacetic Acid, *Hydrochelidonic Acid,* $CO<\begin{smallmatrix}CH_2 . CH_2 . CO_2H\\ CH_2 . CH_2 . CO_2H\end{smallmatrix}$, lævulin-acetic acid, $HOC<\begin{smallmatrix}CH_2 . CH_2COO\\ CH_2CH_2COOH\end{smallmatrix}$, loses water and becomes the γ-dilactone, $C_7H_8O_4$:



$$\begin{matrix}CH_2 . CH_2 . C . CH_2 . CH_2\\ CO — O\ \ O — CO\end{matrix}$$

This is formed when succinic acid is boiled for some time:

$$2C_4H_6O_4 = C_7H_8O_4 + CO_2 + 2H_2O.$$

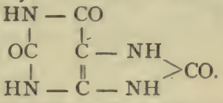
It melts at 75°, and distils without decomposition under reduced pressure. Boiling water, or, better, boiling alkalies cause it to become *acetone diacetic acid*, by absorption of water. This acid is identical with *propion-dicarboxylic acid*, and *hydrochelidonic acid.* The first is obtained by the action of HCl upon furfur-acrylic acid, and the latter by the reduction of chelidonic acid.

Acetone-diacetic acid melts at 143°. Acetyl chloride or acetic anhydride will again convert it into the γ-dilactone. Hydroxylamine changes it to the *oxime*, $C(N . OH)(C_2H_4 . CO_2H)_2$, melting at 129° with decomposition. Its *phenylhydrazone*, $C(N_2H . C_6H_5)(C_2H_4 . CO_2H)_2$, melts at 107° (A. **267**, 48).

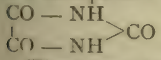
Phoronic Acid, $CO<\begin{smallmatrix}CH_2 . C(CH_3)_2 . CO_2H\\ CH_2 . C(CH_3)_2 . CO_2H\end{smallmatrix}$ (?), melting at 184°, is obtained from the dihydrochloride addition product of phorone (p. 221), by its successive treatment with potassium cyanide and hydrochloric acid (B. **26**, 1173). The corresponding γ-dilactone melts at 134° (A. **247**, 110).

THE URIC ACID GROUP.

Uric acid is a compound of two cyclic urea residues combined with a nucleus of three carbon atoms:

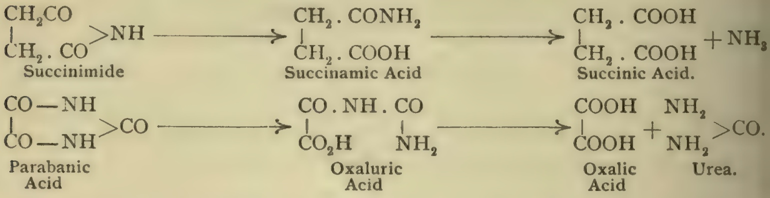


By its oxidation the so-called ureïdes of two dicarboxylic acids—oxalic acid and mesoxalic acid—were made known. The ureïde of a dicarboxylic acid is a compound of an acid radical with the residue, NH . CO . NH ; *e. g.*,



= ureïde of oxalic acid, oxalyl urea, parabanic acid.

They are closely related to the imides of dibasic acids, succinimide (p. 448), and phthalimide, and parabanic acid may, for example, be regarded as a mixed cyclic imide of oxalic and carbonic acids. Like the imides, they possess the nature of an acid, and form salts by the replacement of the imide hydrogen with metals. The imides of dibasic acids are converted by alkalies and alkaline earths into amino-acid salts, which split off ammonia and become salts of dibasic acids. Under similar conditions the ureïde ring is ruptured. At first a so-called *ur*-acid is produced, which finally breaks down into urea and a dibasic acid:



$$\underset{\text{Succinimide}}{\left.\begin{array}{l}CH_2CO\\ \mid\\ CH_2.CO\end{array}\right>NH} \longrightarrow \underset{\text{Succinamic Acid}}{\begin{array}{l}CH_2.CONH_2\\ \mid\\ CH_2.COOH\end{array}} \longrightarrow \underset{\text{Succinic Acid.}}{\begin{array}{l}CH_2.COOH\\ \mid\\ CH_2.COOH\end{array}} + NH_3$$

$$\underset{\text{Parabanic Acid}}{\left.\begin{array}{l}CO-NH\\ \mid\\ CO-NH\end{array}\right>CO} \longrightarrow \underset{\text{Oxaluric Acid}}{\begin{array}{ll}CO.NH.CO & \\ \mid \qquad\quad \mid & \\ CO_2H \quad NH_2 & \end{array}} \longrightarrow \underset{\text{Oxalic Acid}}{\begin{array}{l}COOH\\ \mid\\ COOH\end{array}} + \underset{\text{Urea.}}{\left.\begin{array}{l}NH_2\\ NH_2\end{array}\right>CO.}$$

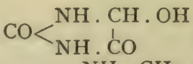
The names of a series of ureïdes having an acid character end in "uric acids,"—*e. g.*, barbituric acid, violuric acid, dilituric acid. These names were constructed before the definition of the ur-acids given above, and it would be better to abandon them and use the ureïde names exclusively,—*e. g.*, malonyl urea, oximidomesoxalyl urea, nitromalonyl urea, etc.

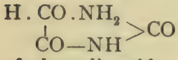
It is the purpose to discuss the urea derivatives of aldehydo- and keton-carboxylic acids, of glyoxalic acid and acetoacetic acid in connection with the ureïdes and "ur" acids of the dicarboxylic acids. These are allantoïn and methyl uracil. The first can also be prepared from uric acid, while the methyl uracil constitutes the starting-out material for the synthesis of uric acid.

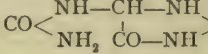
Xanthine, theobromine, theophylline, theïne or caffeïne, and guanine, hypoxanthine, adenine, etc., are related to uric acid.

Ureïdes or Carbamides of Aldehyd- and Keto-mono-carboxylic Acids.

These bodies ally themselves with the ureïdes of the oxyacids, hydantoïn, and hydantoïc acid, which have already been discussed (p. 401).







Glyoxyl Urea and Allanturic Acid, $CO\left<\begin{array}{l}NH.CH.OH\\ \qquad\ \ \mid\\ NH.CO\end{array}\right.$ (?), and $\left.\begin{array}{l}H.CO.NH_2\\ \mid\\ CO-NH\end{array}\right>CO$ (?), as well as **Allantoïn,** $CO\left<\begin{array}{l}NH-CH-NH\\ \qquad\quad \mid\\ NH_2\ \ CO-NH\end{array}\right>CO$, are ureïdes of glyoxylic acid.

Allantoïn is present in the urine of sucking calves, in the allantoïc liquid of cows, and in human urine after the ingestion of tannic acid. It has also been detected in beet-juice (B. 29, 2652). It is produced artificially on heating glyoxalic acid (also mesoxalic acid, $CO(CO_2H)_2$) with urea to 100°.

Allantoïn is formed by oxidizing uric acid with PbO_2,MnO_2, potassium ferricyanide, or with alkaline $KMnO_4$ (B. 7, 227).

Allantoïn crystallizes in glistening prisms, which are slightly soluble in cold water, but readily in hot water and in alcohol. It has a neutral reaction, but dissolves in alkalies, forming salts.

Sodium amalgam converts allantoïn into **glyco-uril,** or **acetylene urea.**

Allanturic acid is obtained from allantoïn on warming with baryta water or with PbO_2, and by the oxidation of glycolyl urea (hydantoïn, p. 401).

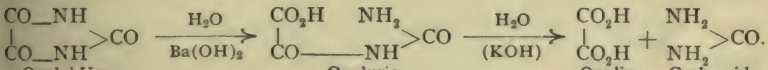
Glyoxyl urea, stout needles dissolving readily in water, is a decomposition product of *oxonic acid*, $C_4H_6N_3O_4$, resulting from the oxidation of uric acid (A. 175, 234).

Pyruvil, $CO<\begin{matrix}NH\,.\,\overset{}{C}(CH_3)\,.\,NH\\ NH_2\,\overset{|}{C}O\ \text{——}\ NH\end{matrix}>CO(?)$, is formed when pyroracemic acid and urea are heated (A. chim. phys. [5] 11, 373) together.

Methyl Uracyl, $CH\begin{matrix}\diagup C(CH_3)\,.\,NH\diagdown\\ \diagdown CO\ \text{——}\ NH\diagup\end{matrix}CO$, is produced when urea acts upon acetoacetic ester. It is the starting-out material for the synthesis of uric acid. To convert it into the latter it is first changed into derivatives of the hypothetical uracyl, $CH\begin{matrix}\diagup CH-NH\diagdown\\ \diagdown CO-NH\diagup\end{matrix}O$. Compare synthesis of uric acid, p. 513 (A. 251, 235).

UREÏDES OR CARBAMIDES OF DICARBOXYLIC ACIDS.

The most important members of this class are parabanic acid and alloxan. They were first obtained by oxidizing uric acid with nitric acid. These cyclic ureïdes by moderated action of alkalies or alkaline earths are hydrolyzed and become "ur"-acids. When the action of the alkalies is energetic, the products are urea and dicarboxylic acids —*e. g.*:



$$\begin{matrix}CO\text{—}NH\\ |\\ CO\text{—}NH\end{matrix}>CO \xrightarrow[Ba(OH)_2]{H_2O} \begin{matrix}CO_2H & NH_2\\ | & \\ CO\text{———} & NH\end{matrix}>CO \xrightarrow[(KOH)]{H_2O} \begin{matrix}CO_2H\\ |\\ CO_2H\end{matrix} + \begin{matrix}NH_2\\ NH_2\end{matrix}>CO.$$

Oxalyl Urea Parabanic Acid — Oxaluric Acid — Oxalic Acid — Carbamide Urea.

Oxalyl Urea, $CO<\begin{matrix}NH\,.\,CO\\ \quad |\\ NH\,.\,CO\end{matrix}$, **Parabanic Acid**, is produced in the oxidation of uric acid and alloxan with ordinary nitric acid (A. 182, 74). It is synthetically prepared by the action of $POCl_3$ upon a mixture of urea and oxalic acid. It is soluble in water and alcohol, but not in ether.

Its *salt* are unstable; water converts them at once into oxalurates. Silver nitrate precipitates the crystalline *disilver salt*, $C_3Ag_2N_2O_3$, from solutions of the acid.

Oxalylmethyl Urea, Methyl Parabanic Acid, $C_3H(CH_3)N_2O_3$, is formed by boiling methyl uric acid, or methyl alloxan, with nitric acid, or by treating theobromine with a chromic acid mixture. It is soluble in ether, and melts at 149.5°.

Oxalyldimethyl Urea, Dimethyl Parabanic Acid, $C_3(CH_3)_2N_2O_3$, **Cholestrophane**, is obtained from dimethyl alloxan and theïne by oxidation, or by heating methyl iodide with silver parabanate. It melts at 145° and distils at 276°.

Oxaluric Acid, $CO<\begin{matrix}NH\,.\,CO\,.\,CO_2H\\ NH_2\end{matrix}$, results from the action of bromine upon parabanic acid. Free oxaluric acid is a crystalline powder, dissolving with difficulty. When boiled with alkalies or water, it decomposes into urea and oxalic acid; heated to 200° with $POCl_3$, it is again changed into parabanic acid.

The *ammonium salt*, $C_3H_3(NH_4)N_2O_4$, and the *silver salt*, $C_3H_3AgN_2O_4$, crystallize in glistening needles.

The *ethyl ester*, $C_3H_3(C_2H_5)N_2O_4$, is formed by the action of ethyl iodide on the silver salt, and has been synthetically prepared by letting ethyl oxalyl chloride act upon urea. It melts at 177°.

Oxaluramide, $CO<\substack{NH . CO . CO . NH_2, \\ NH}$ *Oxalan*, is produced on heating ethyl oxalurate with ammonia, and by fusing urea with ethyl oxamate.

Oxalyl Guanidine, $HN : C<\substack{NHCO \\ | \\ NHCO}$, is formed from oxalic ester and guanidine (B. **26**, 2552; **27**, R. 64).

Malonyl Urea, $CO<\substack{NH . CC \\ NH . CO}>CH_2$, *Barbituric Acid*, is obtained from alloxantin by heating it with concentrated sulphuric acid, and from dibrombarbituric acid by the action of sodium amalgam. It may also be synthetically obtained by heating malonic acid and urea to 100° with $POCl_3$. It crystallizes with two molecules of water in large prisms from a hot solution, and when boiled with alkalies is decomposed into malonic acid and urea.

The hydrogen of CH_2 in malonyl urea can be readily replaced by bromine, NO_2, and the isonitroso-group. The metals in its salts are joined to carbon, and may be replaced by alkyls (B. **14**, 1643; **15**, 2846).

When silver nitrate is added to an ammoniacal solution of barbituric acid, a white silver salt, $C_4H_2Ag_2N_2O_3$, is precipitated. Methyl iodide converts this into **α-Dimethylbarbituric Acid**, $CO<\substack{NH . CO \\ NH . CO}>C(CH_3)_2$. This forms shining laminæ, does not melt at 200°, and sublimes readily. Boiling alkalies decompose it into CO_2, NH_3, and dimethyl malonic acid. Its isomeride, **β-Dimethyl Barbituric Acid**, $CO<\substack{N(CH_3) . CO \\ N(CH\ ) . CO}>CH_2$, is produced from malonic acid and dimethyl urea through the agency of $POCl_3$, or by the reduction of dichlormalonyl dimethyl urea (B. **27**, 3084). It melts at 123°.

Malonyl Guanidine, $NH : C<\substack{NH . CO \\ NH . CO}>CH_2$, from malonic ester and guanidine (B. **26**, 2553), affords derivatives analogous to those of malonyl urea, *e. g.*, *isonitrosomalonyl guanidine*, $NH : C<\substack{NH . CO \\ NH . CO}>C : N . OH$, which hydrogen sulphide reduces to *amidomalonyl guanidine*, $NH : C<\substack{NH . CO \\ NH . CO}>CH . NH_2$. Potassium cyanate converts the latter into *imidopseudo-uric acid*, carbamidomalonyl guanidine, $NH : C<\substack{NH . CO \\ NH . CO}>CH . NH . CO . NH_2$.

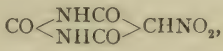
Tartronyl Urea, $CO<\substack{NH . CO \\ NH . CO}>CH . OH$, *Dialuric Acid*, is formed by the reduction of mesoxalyl urea (alloxan) with zinc and hydrochloric acid, and from dibrombarbituric acid by the action of hydrogen sulphide. On adding hydrocyanic acid and potassium carbonate to an aqueous solution of alloxan, potassium dialurate separates but potassium oxalurate remains dissolved:

$$2C_4H_2N_2O_4 + 2KOH = \underset{\text{Potassium Dialurate}}{C_4H_3KN_2O_4} + \underset{\text{Potassium Oxalurate.}}{C_3H_3KN_2O_4} + CO_2$$

Dialuric acid crystallizes in needles or prisms, shows a very acid reaction, and forms salts with 1 and 2 equivalents of the metals. It becomes red in color in the air, absorbs oxygen and passes over into alloxantin, $2C_4H_4N_2O_4 + O = C_8H_4N_4O_7 + 2H_2O$.

Tartronyl Dimethyl Urea, $CO{<}\begin{matrix}N(CH_3)\,.\,CO\\N(CH_3)\,.\,CO\end{matrix}{>}CH\,.\,OH$, melts at about 170° with decomposition (B. **27**, 3082).

Nitromalonyl Urea, Nitrobarbituric Acid, Dilituric Acid:

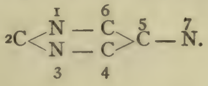


$$CO{<}\begin{matrix}NHCO\\NHCO\end{matrix}{>}CHNO_2,$$

is obtained by the action of fuming nitric acid upon barbituric acid and by the oxidation of violuric acid (B. **16**, 1135). It crystallizes with three molecules of water and can exchange three hydrogen atoms for metals. *Nitromalonyl Dimethyl Urea* melts at 148° (B. **28**, R. 321).

Amidomalonyl Urea, Amidobarbituric Acid, $CO{<}\begin{matrix}NH\,.\,CO\\NH\,.\,CO\end{matrix}{>}CHNH_2$ (Uramil. Dialuramide, Murexan), is obtained in the reduction of nitro- and isonitrosobarbituric acid with hydriodic acid; by boiling thionuric acid with water, and by boiling alloxantin with an ammonium chloride solution. Alloxan remains in solution, while uramil crystallizes out. It is only slightly soluble in water, and crystallizes in colorless, shining needles, which redden on exposure. Murexide (p. 510) is produced when the solution is boiled with ammonia. Nitrous acid converts uramil into alloxan.

Methyl Uramils.—In order to indicate the positions of the methyl groups, the uramil carbon and nitrogen atoms are marked with the numbers 1 to 7, according to the following diagram, which shows the numbering of the uric acid nucleus (p. 511):



$$^{2}C{<}\begin{matrix}\overset{1}{N}-\overset{6}{C}\\\underset{3}{N}-\underset{4}{C}\end{matrix}{>}\overset{5}{C}-\overset{7}{N}.$$

1.3-*Dimethyl Uramil,* $CH{<}\begin{matrix}N(CH_3)\,.\,CO\\N(CH_3)\,.\,CO\end{matrix}{>}CH\,.\,NH_2$, melts with decomposition at 200°. It is produced when hydrochloric acid acts upon *ammonium dimethyl thionurate*, $CO[N(CH_3)CO]_2\,.\,CH\,.\,NH\,.\,SO_3NH_4 + 2H_2O$—the product resulting from the action of ammonia, sulphur dioxide, and ammonium carbonate upon a solution of dimethyl alloxan (B. **27**, 3088).

1.3.7-*Trimethyl Uramil,* $CO{<}\begin{matrix}N(CH_3)\,.\,CO\\N(CH_3)\,.\,CO\end{matrix}{>}CH\,.\,NH\,.\,CH_3$, decomposes when rapidly heated at 200°. It is formed from dimethyl alloxan by the action of methylamine sulphite, and then hydrochloric acid (B. **30**, 564).

Amidomalonyl Guanidine, see Methyl Guanidine, p. 506.

Pseudouric Acid, *Carbamidomalonyl Urea,* $CO{<}\begin{matrix}NH\,.\,CO\\NH\,.\,CO\end{matrix}{>}CHNH\,.\,CONH_2$. Uramil and urea heated to 180° yield the ammonium salt of this acid. The potassium salt is obtained from uramil or from murexide and potassium cyanate.

Methyl Pseudouric Acids are obtained from the corresponding methyl uramils, which for this purpose need not be isolated, when they are treated with potassium cyanate. When heated to 150° with fusing oxalic acid, or when boiled with hydrochloric acid, they lose water, and yield the corresponding uric acids. In this manner the following bodies have been prepared:

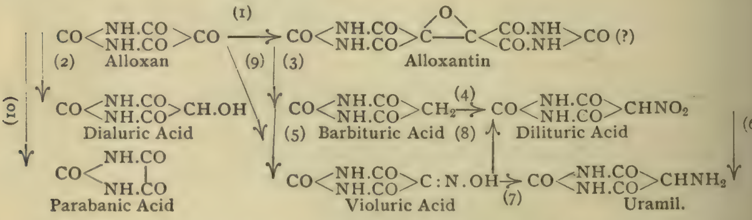
7-*Monomethyl Pseudo-uric Acid*, 1.3-*Dimethylpseudo-uric Acid*, 1.3.7-*Trimethyl Pseudo-uric Acid* (B. **30**, 559), 2-*Imidopseudo-uric Acid*, Carbamidomalonyl Guanidine, p. 506.

Thiouramil, $CO{<}\begin{matrix}NH\,.\,C(SH)\\NH\,.\,CO\end{matrix}{\gtrless}C\,.\,NH_2$, results when a solution of potassium urate is heated with ammonium sulphide to 155-160° (B. **28**, R. 909; A. **288**, 157). It is a strong acid. Its solution imparts an orange color to a pine chip. It gives the murexide test (p. 510). Nitric acid oxidizes it to sulphuric acid and alloxan. **Thiodimethyl Uramil,** $CO<\substack{N(CH_3).C(SH)\\N(CH_3).CO}>NH_2$, **β-Thiopseudouric Acid** $CO<\substack{NH.C(SH)\\NH.CO}>C.NHCO.NH_2$, is obtained from thiouramil and potassium cyanate (A. 288, 171).

Alloxan, Mesoxalyl Urea, $CO<\substack{NH.CO\\NH.CO}>C<\substack{OH\\OH} + 3H_2O$, is produced by the careful oxidation of uric acid, or alloxantin with nitric acid, chlorine, or bromine. Alloxan crystallizes from warm water in long, shining, rhombic prisms, with 4 molecules of H_2O. When exposed to the air they effloresce with separation of $3H_2O$. The last molecule of water is intimately combined (p. 497), as in mesoxalic acid, and does not escape until heated to 150°.

Alloxan is easily soluble in water, has a very acid reaction, and possesses a disagreeable taste. The solution placed on the skin slowly stains it a purple red. Ferrous salts impart a deep indigo blue color to the solution. When hydrocyanic acid and ammonia are added to the aqueous solution, the alloxan decomposes into CO_2, dialuric acid, and oxaluramide (p. 506), which separates as a white precipitate (reaction for detection of alloxan).

Alloxan is the starting-point for the preparation of numerous transposition products (Baeyer, A. 127, 1, 199; 130, 129), which have in part already received mention, and some of which will be discussed after alloxan. These genetic relationships are expressed in the following diagram:



(1) Reducing agents, *e. g.*, hydriodic acid ($SnCl_2$, H_2S, Zn and hydrochloric acid), convert alloxan in the cold into *alloxantin* (p. 509); (2) on warming, into *dialuric acid* (p. 506). (3) Alloxantin digested with concentrated sulphuric acid becomes *barbituric acid* (p. 506); (4) fuming nitric acid changes it to *dilituric acid;* (5) and with potassium nitrite it yields *violuric acid.* (6) (7) Uramil results from the reduction of dilituric acid and violuric acid. (8) Dilituric acid is formed when violuric acid is oxidized. (9) Hydroxylamine converts alloxan into its oxime—violuric acid. (10) Boiling dilute nitric acid oxidizes alloxan to parabanic acid and CO_2.

The primary alkali sulphites unite with alloxan just as they do with mesoxalic acid, and we can obtain crystalline compounds, *e. g.*, $C_4H_2N_2O_4 . SO_3KH + H_2O$. Pure alloxan can be preserved without undergoing decomposition, but in the presence of even minute quantities of nitric acid it is converted into alloxantin. Alkalies, lime or baryta water change it to alloxanic acid, even when acting in the cold. Its aqueous solution undergoes a gradual decomposition (more rapid on heating) into alloxantin, parabanic acid, and CO_2. For the action of o-diamines upon alloxan, see B. 26, 540; for that of pyrazolon derivatives, see A. 255, 230.

Methyl Alloxan, $CO<\substack{N(CH_3) - CO\\NH - CO}>CO$, is produced by the oxidation of methyl uric acid.

Dimethyl Alloxan, $CO<^{N(CH_3)-CO}_{N(CH_3)-CO}>CO$, is produced when aqueous chlorine (hydrochloric acid and $KClO_3$) acts on theïne, and by the careful oxidation of tetramethyl alloxantin (B. **27**, 3082). When it is boiled with nitric acid, methyl and dimethylparabanic acids are formed.

Dibrommalonyl Urea, *Dibrombarbituric Acid,* $CO<^{NHCO}_{NHCO}>CBr_2$, results when bromine acts upon barbituric acid, nitro-, amido- and isonitroso-barbituric acids.

Oximidomesoxalyl Urea, *Isonitrosobarbituric Acid, Violuric Acid,*

$$CO<^{NHCO}_{NHCO}>C=NOH,$$

the oxime of alloxan, the first known "ketoxime," is obtained by the action of potassium nitrite on barbituric acid, and of hydroxylamine upon alloxan. It unites with metals to form blue, violet, or yellow colored salts. When heated with the alkalies, it breaks down into urea and isonitrosomalonic acid (p. 498). *Oximidomesoxalyl Dimethyl Urea* melts at 141° (B. **28**, 3142; R. 912).

Alloxan phenylhydrazone melts with decomposition at 295–300° (B. **24**, 4140).

Alloxan semicarbazide decomposes at 260° (B. **30**, 131).

Thionuric Acid, $CO<^{NH.CO}_{NH.CO}>C<^{NH_2}_{SO_3H}$, sulphamidobarbituric acid, is obtained by heating isonitrosobarbituric acid or alloxan with ammonium sulphite. *Dimethyl Thionuric Acid,* see B. **27**, 3086.

Alloxanic Acid, $CO<^{NH.CO.CO.CO.OH}_{NH_2}$. If baryta water be added to a warm solution of alloxan, as long as the precipitate which forms continues to dissolve, barium alloxanate, $C_4H_2BaN_2O_5 + 4H_2O$, will separate out in needles when the solution cools. To obtain the free acid, decompose the barium salt with sulphuric acid and evaporate at a temperature of 30–40°. A mass of crystals is obtained by this means. Water dissolves them easily. Alloxanic acid is a dibasic acid, inasmuch as both the hydrogen of carboxyl and of the imide group can be exchanged for metals. When the salts are boiled with water, they decompose into urea and mesoxalates (p. 497).

Diureïdes.—Parabanic acid, alloxan, and dimethyl alloxan are ureïdes. Two molecules of each unite, and by reduction the diureïdes result. They are oxalantin, alloxantin, and amalic acid. These probably sustain the same relation to the simple ureïdes that tetramethyl ethylene oxide (p. 299), the anhydride of pinacone, bears to acetone.

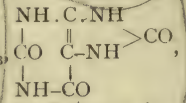
Oxalantin, $C_6H_6N_4O_6$, **Leucoturic Acid,** is obtained by the reduction of parabanic acid.

Alloxantin, $CO<^{NH.CO}_{NH.CO}>\overset{/\,O\,\backslash}{C\text{—}C}<^{CO.NH}_{CO.NH}>CO + 3H_2O$ (?), is obtained by reducing alloxan with $SnCl_2$, zinc and hydrochloric acid, or H_2S in the cold; or by mixing solutions of alloxan and dialuric acid. It can also be obtained from convicin, a substance from *Vicia Faba minor* and *Vicia sativa*, when they are heated with sulphuric or hydrochloric acid (B. **29**, 2106). It is most readily prepared by warming uric acid with dilute nitric acid (A. **147**, 367). It crystallizes from hot H_2O in small, hard prisms with $3H_2O$ and turns red in air containing ammonia. Its solution has an acid reaction; ferric chloride and ammonia give it a deep blue color, and baryta water produces a violet precipitate, which on boiling is converted into a mixture of barium alloxanate and dialurate. On boiling alloxantin with dilute sulphuric acid, it changes to the ammonium salt of *hydurilic acid*, $C_8H_6N_4O_6 + 2H_2O$. It combines with cyanamide, forming *isouric acid* (B. **29**, 2107).

Tetramethyl Alloxantin, $C_8(CH_3)_4N_4O_7$, **Amalic Acid**, is formed by the action of nitric acid or chlorine water upon theïne, or, better, by the reduction of dimethyl alloxan (see above) with hydrogen sulphide (A. **215**, 258). Its deportment is similar to that of alloxan.

Purpuric Acid, $C_8H_5N_5O_6$, is not known in the free state, because as soon as it is liberated from its salts by mineral acids it immediately decomposes into alloxan and uramil. The *ammonium salt*, $C_8H_4(NH_4)N_5O_6 + H_2O$, is the dye-stuff *murexide*. This is formed by heating alloxantin to 100° in ammonia gas; by mixing ammoniacal solutions of alloxan and uramil; and by evaporating uric acid with dilute nitric acid and pouring ammonia over the residue (murexide reaction).

Murexide separates from the solution on cooling. It forms four-sided plates or prisms with one molecule of H_2O, and has a gold-green color. It dissolves in water with a purple-red color, but is insoluble in alcohol and ether. It dissolves with a dark blue color in potash; on boiling, NH_3 is disengaged and the solution decolorized.

Uric Acid, $C_5H_4N_4O_3$, 

$$\begin{array}{l} \mathrm{NH.C{-}NH} \\ \;|\qquad \| \qquad\quad >\mathrm{CO} \\ \mathrm{CO}\;\;\; \mathrm{C{-}NH} \\ \;|\qquad | \\ \mathrm{NH{-}CO} \end{array}$$

, is a white, crystalline, sandy powder, discovered by Scheele in 1776 in urinary calculi. It occurs in the juice of the muscles, in the blood and in the urine, especially of the carnivoræ, the herbivoræ separating hippuric acid; also, in the excrements of birds, reptiles and insects. When urine is exposed for a while to the air, uric acid separates; this also occurs in the organism (formation of gravel and joint concretions) in certain abnormal conditions.

History.—Liebig and Wöhler (1826) showed that numerous transposition products could be obtained from uric acid. Their relationships and constitution were chiefly explained by Baeyer in 1863 and 1864. In consequence of certain experiments of A. Strecker, Medicus (1875) proposed the structural formula given above for the acid. This was conclusively proven by E. Fischer in his investigation of the methylated uric acids.

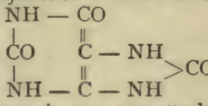
The results derived from analysis were confirmed by the synthesis made in 1888 by R. Behrend and O. Roosen. They proceeded from acetoacetic ester and urea (p. 513). Horbaczewski (1882–1887) had previously made syntheses of uric acid at elevated temperatures, but obtained poor yields. They consisted in melting together glycocoll, trichlorlactamide, etc., with urea. No clue as to the constitution of the acid could be deduced from these. In 1895 E. Fischer and Lorenz Ach showed how pseudouric acid, previously synthesized by A. Baeyer, could by fusion with oxalic acid be converted into uric acid.

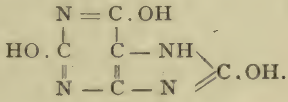
Preparation.—Uric acid is best prepared from guano or the excrements of reptiles.

Properties.—Uric acid is a shining, white powder. It is odorless and tasteless, insoluble in alcohol and ether, and dissolves with difficulty in water; 1 part requires 15,000 parts water of 20° for its solution, and 1800 parts at 100°. Its solubility is increased by the presence of salts like sodium phosphate and borate. Water precipitates it from its solution in concentrated sulphuric acid. On evaporating uric acid to dryness with nitric acid, we obtain a yellow residue, which assumes a purple-red color if moistened with ammonia, or violet with caustic potash or soda (murexide reaction, p. 510). Uric acid heated with ammonium sulphide changes to thiouramil (p. 507). Heat decomposes uric acid into NH_3, CO_2, urea, and cyanuric acid.

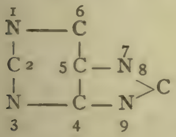
Uric acid is a weak dibasic acid. It forms primary salts with the alkaline carbonates. The secondary alkali salts are obtained by dissolving the acid in the hydroxides of potassium and sodium; they are changed to the primary form by CO_2 and water. When CO_2 is conducted through the alkaline solution, the primary salts are precipitated.

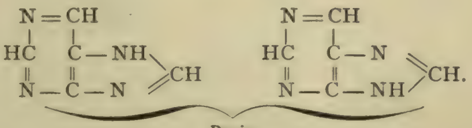
The *primary salt*, $C_5H_3KN_4O_3$, dissolves in 800 parts of water at 20°. The *primary sodium salt* is more insoluble. The *primary ammonium salt* is a sparingly soluble powder. The *lithium salt* (Lipowitz) is much more soluble (in 368 parts of water at 19°) (A. **122**, 241), hence lithium mineral waters are used in such diseases where there is an excessive secretion of uric acid. This salt is, however, greatly surpassed by the *piperazine salt*, $C_5H_4N_4O_3 . NH<\begin{matrix}CH_2 . CH_2\\CH_2 . CH_2\end{matrix}>NH$ (Finzelberg), which dissolves in 50 parts of water at 17° (B. **23**, 3718). The *lysidine* or the *methylglyoxalidine salt* (Ladenburg) is even more soluble (one part in 6 parts of water; B. **27**, 2952).

Methyl Uric Acids.—The four hydrogen atoms in uric acid can be replaced by methyl. In all methyl uric acids the methyl groups are linked to nitrogen; this is also the case with tetramethyl uric acid, and in conjunction with the decompositions and synthesis of uric acid, argues for the formula,  without, however, in the light of our present representations, in any way attaching to formulas such as follow, or any like them:



To indicate the position of the methyl groups in the methyl uric acids and the constitution of other bodies containing the same hetero-twin ring, E. Fischer suggested that the carbon and nitrogen atoms of the nucleus contained in uric acid and bodies related to it be numbered, and that the hydrogen compound of the nucleus, $C_5N_4H_4$, which could have two formulas, should be called "*purin*":





Purin.

Methyl uric acids are obtained by treating urate and methyl urate of lead (also the potassium salts) with methyl iodide. The corresponding pseudouric acids (p. 507) split off water and yield them. Three mono-, four di-, and two tri-methyl uric acids are known in addition to tetramethyl uric acid.

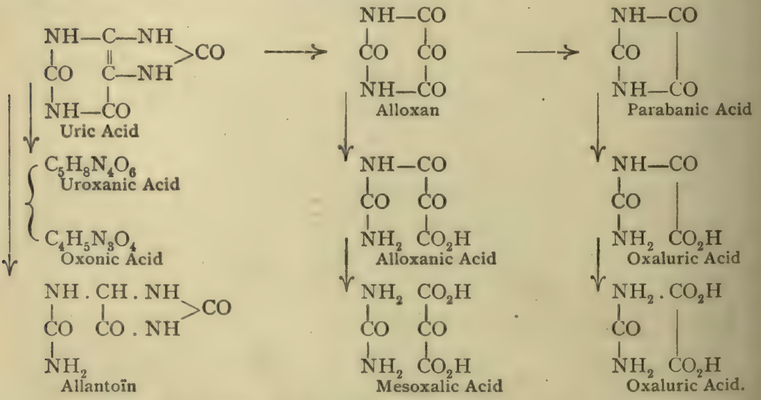
9-*Methyl Uric Acid* (β) is formed together with 1- or 3-*Methyl Uric Acid* (a) when lead urate is treated with methyl iodide in ether at 150–160°. The first is converted by nitric acid into alloxan, the second into methyl alloxan. When heated with hydrochloric acid both pass into glycocoll. 7-*Methyl Uric Acid* (γ-) is obtained from 7-methyl pseudouric acid (p. 507).

1.9-or 3.9-*Dimethyl Uric Acid* (a-) is made from basic lead urate and methyl iodide. 7.9-*Dimethyl Uric Acid* (β-) see B. 17, 1780.

1.3-*Dimethyl Uric Acid* (γ-) is obtained from 1.3-dimethyl pseudouric acid (p. 507); see also theophyllin (p. 515). 3.7-*Dimethyl Uric Acid* (δ) is formed from 7-methyl uric acid; see also theobromine (p. 514). 3.7.9-*Trimethyl Uric Acid* (a-) is derived from 7.9-dimethyl uric acid. 1.3.7-*Trimethyl Uric Acid*, from 1.3.7-trimethyl pseudouric acid (a-), is identical with hydroxycaffeïn (B. 30, 567). *Tetramethyl Uric Acid* is made from trimethyl urate of potassium and methyl iodide.

OXIDATION OF URIC ACID.

Mesoxalyl urea or alloxan and oxalyl urea or parabanic acid are produced when uric acid is oxidized with ordinary nitric acid. When the acid is carefully oxidized either with cold nitric acid or with potassium chlorate and hydrochloric acid, it yields mesoxalyl urea and urea. Allantoïn is produced when potassium permanganate, or iodine in caustic potash, acts upon the acid (B. **27**, R. 902). When air or potassium permanganate acts upon the alkaline solution of uric acid (B. **27**, R. 887; **28**, R. 474), *uroxanic acid*, $C_5H_8N_4O_6$, is produced; this the alkali changes to *oxonic acid*, $C_4H_5N_3O_4$. These are two bodies whose constitution has not yet been made clear. These reactions suggest the following diagram, in which the breaking-down of alloxan and parabanic acid is considered:

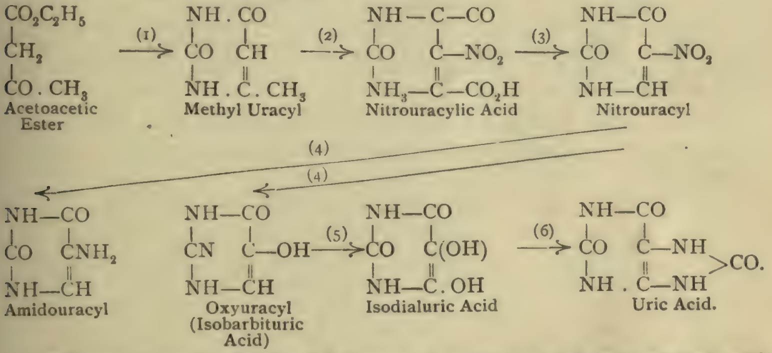


One of the two isomeric monomethyl uric acids, when oxidized, yields monomethyl alloxan and urea, the other alloxan and monomethyl urea. These reactions are readily understood if we assume the constitutional formula of uric acid to be as indicated above (E. Fischer, B. **17**, 1785).

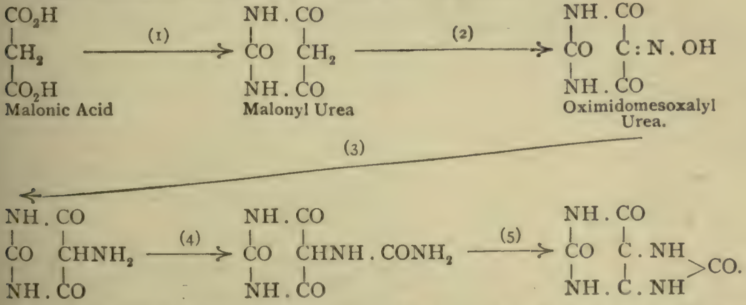
Uric acid is the diureïde of the hypothetical body, $CO=C(OH).CO_2H$, or $C(OH)_2=C(OH)-CO_2H$—the pseudo-form of the half-aldehyde of mesoxalic acid, $CHO.CO.CO_2H$, which has not yet been prepared.

SYNTHESIS OF URIC ACID: (1) FROM ACETOACETIC ESTER; (2) FROM MALONIC ACID.

(1) **From Acetoacetic Ester:** (1) Acetoacetic ester and urea unite to *β-uramido-crotonic ester.* When this is saponified with alkali it yields an acid which, in a free state, splits off water and becomes a cyclic ureïde—*methyl uracyl.* (2) Nitric acid converts the latter into *nitrouracyl carboxylic acid,* (3) whose potassium salt when boiled with water loses a molecule of carbonic acid, and becomes the potassium salt of *nitrouracyl.* (4) The reduction of the latter with tin and hydrochloric acid gives in part *amidouracyl,* and in part oxyuracyl or *isobarbituric acid.* (5) Bromine water oxidizes the latter to *isodialuric acid,* which when heated (6) with urea and sulphuric acid yields *uric acid* (A. 251, 235).

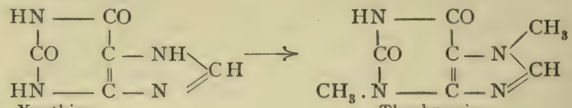


(2) **From Malonic Acid:** (1) Urea and malonic acid heated to 100° with $POCl_3$ yield malonyl urea, which (2) nitrous acid converts into oximido-mesoxalyl urea or violuric acid. (3) When the latter is reduced, amidomalonyl urea or uramil results. (4) This is changed by potassium cyanate into pseudouric acid. (5) On withdrawing water from pseudouric acid by means of molten oxalic acid or boiling hydrochloric acid, *uric acid* results (B. 30, 559):

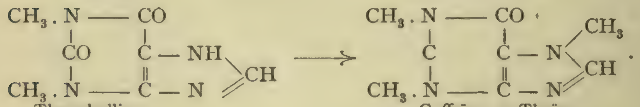


Since alloxan and dimethyl alloxan yield methylated pseudouric acids, methylated uric acids can also be synthesized in this way.

Xanthine Group.—Guanine, xanthine, hypoxanthine, and carnine stand in close relation to uric acid. Like it, they occur as products of the metabolism of the animal organism. Xanthine and hypoxanthine occur in the extract of tea. Theobromine, theophylline, and theïne or caffeïne—methyl derivatives of xanthine—are found in the vegetable kingdom:



Xanthine Theobromine



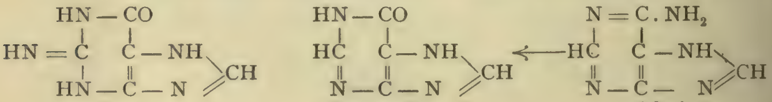
Theophylline Caffeïne, or Theïne.

The breaking-down of xanthine into alloxan and urea, and of caffeïne into dimethyl alloxan and methyl urea, by means of potassium chlorate and hydrochloric acid, are particularly important in the explanation of their constitution.

Nitrous acid converts guanine into xanthine, and by decomposition yields guanidine, $(NH_2)_2C:NH$ (p. 411), hence it must be regarded as xanthine in which a guanidine residue takes the place of a urea-residue; *i. e.*, the oxygen of a CO group is replaced by imide NH.

Adenine bears the same relation to hypoxanthine that guanine sustains to xanthine, inasmuch as it is converted by nitric acid into hypoxanthine.

The xanthine group compounds occur in beet juice (B. **29**, 2649):



Guanine Hypoxanthine Adenine.

Xanthine (see constitutional formula above) occurs in slight amounts in many animal secretions, in the blood, in urine, in the liver, in some forms of calculi, and in tea extract. It results from the action of nitrous acid upon guanine (A. **215**, 309). It is a white, amorphous mass, somewhat soluble in boiling water, and combines with both acids and bases. It is readily soluble in boiling ammonia; silver nitrate precipitates $C_5H_2Ag_2N_4O_2 + H_2O$ from its solution. The corresponding lead compound yields theobromine (dimethyl xanthine) when heated to 100° with methyl iodide. When xanthine (analogous to caffeïne, page 515) is warmed with potassium chlorate and hydrochloric acid it splits into alloxan and urea.

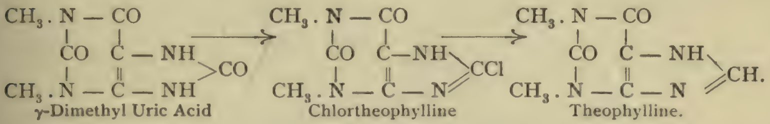
Heteroxanthine, 7-*methyl xanthine*, occurs in small quantities in urine (B. **18**, 3406), and is formed from theobromine by the splitting off of methyl (B. **28**, 1118; **29**, R. 47; **30**, 554).

Theobromine, 3.7-*dimethyl xanthine*, occurs in cocoa-beans (from *Theobroma Cacao*) and is prepared by introducing methyl into xanthine (see above).

Theobromine is a crystalline powder with a bitter taste and dissolves with difficulty in hot water and alcohol, but rather easily in ammonium hydroxide. It sublimes (about 290°) without decomposition, when it is carefully heated. It has a neutral reaction, but yields crystalline salts on dissolving in acids; much water will decompose these. Silver nitrate precipitates the compound, $C_7H_7AgN_4O_2$, in crystalline form from the ammoniacal solution after protracted heating. When this salt is heated with methyl iodide it yields methyl theobromine, $C_7H_7(CH_3)N_4O_2$, *i. e.*, caffeïne.

Paraxanthine, 1.7 *dimethyl xanthine*, occurs in urine (B. **18**, 3406). It can also be prepared from theobromine, from which a methyl group can easily be split off and again introduced in another position. It passes by methylation into caffeïne (B. **30**, 554).

Theophylline, 1.3 *dimethyl xanthine*, melting at 264°, was discovered in 1888 by Kossel in tea extract. By the action of methyl iodide upon silver theophylline he obtained caffeïne (B. **21**, 2164). Theophylline has been synthetically prepared from 1.3- or γ-dimethyl uric acid by its conversion with PCl_5 into *chlortheophylline*. This melts at about 300° with decomposition; hydriodic acid reduces it to theophylline (E. Fischer, B. **30**, 553):



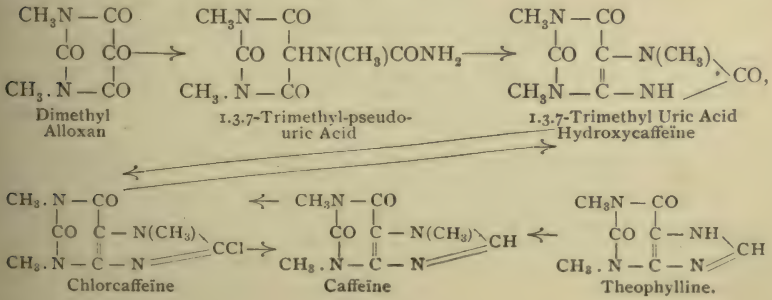
Caffeïne, Coffeïne, Theïne, 1.3.7-*trimethyl xanthine*, occurs in the leaves and beans of the coffee tree (½ per cent.), in tea (2–4 per cent.), in Paraguay tea (from *Ilex paraguayensis*), in guarana (about 5 per cent.), the roasted pulp of the fruit of *Paullinia sorbilis*, and in the cola nuts (3 per cent.). It is also found in minute quantities in cocoa. It is used in medicine as a nerve stimulant.

Caffeïne consists of long, silky needles with one molecule of water; they are only slightly soluble in cold water and alcohol. At 100° it loses its water, and melts at 233°.

It has a feeble bitter taste, and forms salts with the strong mineral acids; water readily decomposes them. On evaporating a solution of chlorine water containing traces of caffeïne we get a reddish-brown spot, which acquires a beautiful violet-red color when dissolved in ammonia water.

Sodium hydroxide converts theïne into *caffeïdine carboxylic acid*, $C_7H_{11}N_4O.CO_2H$, which readily decomposes into CO_2 and *caffeïdine*, $C_7H_{12}N_4O$ (B. **16**, 2309). For other caffeïne derivatives (apocaffeïne, caffuric acid, caffolin) see A. **215**, 261, and **228**, 141.

Chlorine water breaks caffeïne up into dimethyl alloxan and methyl urea (p. 399). Chlorine and bromine convert caffeïne into *chlorcaffeïne*, melting at 180°, and *bromcaffeïne*, melting at 206°. Zinc dust reduces both of them to caffeïne. Alcoholic potash changes them to *ethoxycaffeïne*, melting at 140°. The latter is decomposed by hydrochloric acid into ethyl chloride and *hydroxycaffeïne*, melting at 345°. This is identical with 1.3.7-*trimethyl uric acid*. PCl_5 converts hydroxycaffeïne into chlorcaffeïne. Proceeding from dimethyl alloxan, 1.3.7-trimethyl uric acid may be synthetically made, and from this caffeïne through chlorcaffeïne. Furthermore, the lower homologues of caffeïne—theobromine and theophylline—can be synthesized, and by introducing methyl into them caffeïne will result. This, then, is an additional synthesis of caffeïne (E. Fischer, B. **30**, 549):

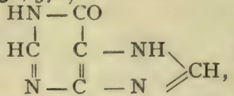


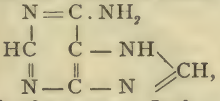
Guanine, $C_5H_5N_5O$, occurs in the pancreas of some animals and very abundantly in guano.

Guanine is an amorphous powder, insoluble in water, alcohol and ether. It yields crystalline salts with 1 and 2 equivalents of acid, *e. g.*, $C_5H_5N_5O . 2HCl$. It also forms crystalline compounds with bases. Silver nitrate gives a crystalline precipitate, $C_5H_5N_5O . NO_3Ag$.

Nitrous acid converts guanine into xanthine. Potassium chlorate and hydrochloric acid decompose it into parabanic acid, guanidine and CO_2 (p. 411).

2-Amino-6.8-dioxypurin is obtained from 2-imidopseudouric acid (p. 507) and from bromguanine (B. 30, 570).

Sarcine, *Hypoxanthine*,  is a constant attendant of xanthine in the animal organism, and is distinguished principally by the difficult solubility of its hydrochloride. It consists of needles not very soluble in water, but dissolved by alkalies and acids. Silver nitrate precipitates the compound $C_5H_2Ag_2N_4O + H_2O$ from ammoniacal solutions. Dimethyl hypoxanthine splits into methylamine and sarcosine when it is heated with hydrochloric acid (p. 317) (B. 26, 1914).

Adenine,  polymeric with hydrogen cyanide, has been isolated from beef pancreas. It also occurs in tea extract. It crystallizes in leaflets with pearly lustre. It has three molecules of water of crystallization. At 54° the salt becomes white in color, owing to loss of water. Nitrous acid converts it into hypoxanthine, and hydrochloric acid at 180–200° converts it into glycocoll, ammonia. formic acid, and CO_2 (Kossel, B. 23, 225; 26, 1914).

Carnine, $C_7H_8N_4O + H_2O$, has been found in the extract of beef. It is a powder, rather easily soluble in water, and forms a crystalline compound with hydrochloric acid. Bromine water or nitric acid converts carnine into sarcine.

14. TRICARBOXYLIC ACIDS.

A. PARAFFIN TRICARBOXYLIC ACIDS.

(*a*) *Tricarboxylic Acids with Two or Three Carboxyls Attached to the Same Carbon Atom.*

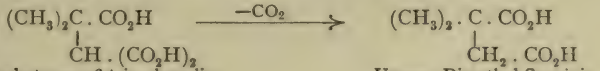
Formation.—(1 *a*) By the action of the halogen fatty-acid esters on the sodium compounds of malonic esters, $CHNa(CO_2R')_2$ and alkylic malonic esters, $R'. CNa(CO_2R')_2$—*e. g.*, chlorcarbonic ester, chloracetic ester, α-brompropionic ester, α-brombutyric ester, α-bromisobutyric ester. (1 *b*) The tricarboxylic esters, resulting in this way from sodium malonic ester, still contain a hydrogen of the CH_2-group of malonic ester, and can be acted upon anew with sodium and alkyl iodides. They then yield the same esters, which are obtained by starting with the monoalkylic malonic esters.

(2) By the addition of sodium malonic esters to unsaturated carboxylic esters, *e. g.*, crotonic ester (B. 24, 2888; C. 1897, I, 28).

(3) Also by the gradual saponification of tetracarboxylic esters, containing two carboxyl groups attached to the same carbon atom, which split off carbon dioxide and yield tricarboxylic esters (B. 16, 333; 23, 633; A. 214, 58).

(4) By heating the best adapted ketone tricarboxylic esters (B. 27, 797), when a loss of CO occurs.

Like malonic acid, these tricarboxylic acids readily break down with the elimination of CO_2. They then become succinic acids, *e. g.*:



$$\begin{array}{l}(CH_3)_2C . CO_2H\\ \quad | \\ \quad CH . (CO_2H)_2\end{array} \xrightarrow{-CO_2} \begin{array}{l}(CH_3)_2 . C . CO_2H\\ \qquad | \\ \qquad CH_2 . CO_2H\end{array}$$

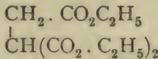
Isobutane-*aaβ*-tricarboxylic Acid **Unsym. Dimethyl Succinic Acid.**

For the saponification of tricarboxylic esters consult B. **29**, 1867.

Formyl Tricarboxylic Ester, Methenyl Tricarboxylic Ester, $CH(CO_2C_2H_5)_3$, is obtained from sodium malonic ester, $CHNa(CO_2 . C_2H_5)_2$, and ethyl chlorcarbonate (B. **21**, R. 531); it melts at 29°, and boils at 253°.

Cyanmalonic Ester, $CH(CN)(CO_2R)_2$, results from the action of cyanogen chloride upon sodium malonic ester. It volatilizes without decomposition under greatly reduced pressure. It has a very acid reaction, and decomposes the alkaline carbonates, forming salts, like $CNa(CN)(CO_2R)_2$ (B. **22**, R. 567).

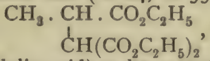
Cyanoform, $CH(CN)_3 + CH_3OH$ (?), melts with decomposition at 214°. Sodium cyanoform is produced when cyanogen chloride acts upon malonitrile and sodium ethylate (B. **29**, 1171).



Ethenyl Tricarboxylic Ester, $\begin{array}{l}CH_2 . CO_2C_2H_5\\ | \\ CH(CO_2 . C_2H_5)_2\end{array}$, is obtained from sodium ethyl malonate and the ester of chloracetic acid. It boils at 278°. Chlorine converts it into **Chlorethenyl Tricarboxylic Ester,** $C_2H_2Cl(CO_2 . C_2H_5)_3$. This boils at 290°, and when heated with hydrochloric acid, yields carbon dioxide, hydrochloric acid, alcohol, and fumaric acid; when saponified with alkalies, carbon dioxide and malic acid are the products (A. **214**, 44).

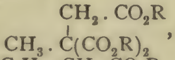
Unsym. **Dimethyl Cyansuccinic Ester,** B. **27**, R. 506.

Methyl *a*-Cyansuccinic Ester, $(CO_2CH_3)CH_2CH(CN)CO_2CH_3$, is obtained from methyl cyanacetic ester and chloracetic ester (B. **24**, R. 557).

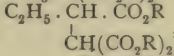


Propane-*aaβ*-tricarboxylic Ester, $\begin{array}{l}CH_3 . CH . CO_2C_2H_5\\ \quad\;\; | \\ \quad\;\; CH(CO_2C_2H_5)_2\end{array}$, boils at 270°.

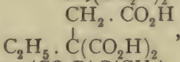
The free acid (isomeric with tricarballylic acid) melts at 146°, and breaks down into carbon dioxide and pyrotartaric acid.



Propane-*aββ*-tricarboxylic Ester, $\begin{array}{l}\qquad CH_2 . CO_2R\\ \qquad | \\ CH_3 . C(CO_2R)_2\end{array}$, boils at 273°.



n-Butane-*aaβ*-tricarboxylic Ester, $\begin{array}{l}C_2H_5 . CH . CO_2R\\ \qquad | \\ \qquad CH(CO_2R)_2\end{array}$, boils at 278°.



n-Butane-*aββ*-tricarboxylic Ester, $\begin{array}{l}\qquad CH_2 . CO_2H\\ \qquad | \\ C_2H_5 . C(CO_2H)_2\end{array}$, boils at 281°.

Isobutane-*aaβ*-tricarboxylic Ester, $(CO_2R)C(CH_3)_2 . CH(CO_2R)_2$, boils at 277°. Compare B. **23**, 648.

In these formulas R represents C_2H_5.

***a*-Cyanglutaric Ester** (B. **27**, R. 506).

a-Alkyl-a-Carboxy-glutaric Ester, see A. **292**, 209; C. 1897, I, 28.

ββ-Dimethyl-a-Carboxy-glutaric Ester, see ββ-Dimethyl glutaric acid, p. 454.

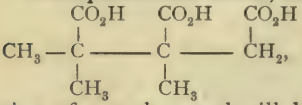
(*b*) *Tricarboxylic Acids with the Carboxyl Groups Attached to Three Carbon Atoms.*

Tetra- and penta-carboxylic acids, containing one or two pairs of CO_2H-groups attached to the same carbon atom split off carbon dioxide, and numerous representatives of the class have been prepared (B. **24**, 307, 2889; **25**, R. 746).

Tricarballylic Acid, $CH_2 . (CO_2H) . CH(CO_2H)CH_2(CO_2H)$, crystallizes in rhombic prisms, which dissolve easily in water, and melt at 162–164°. It is obtained: (1) By heating tribromallyl with potassium cyanide and decomposing the tricyanide with potash; (2) by oxidizing diallyl acetic acid (p. 289); (3) by acting upon ethyl aceto-succinate with sodium and the ester of chloracetic acid, then saponifying the aceto-tricarballylic ester (see this); (4) by the decomposition of propane-*ααβγ*- and *αββγ*-tetracarboxylic ester (B. **24**, 307, 2889; **29**, 1281); (5) by the action of nascent hydrogen upon aconitic acid, $C_6H_6O_6$ (B. **22**, 2921), and by the reduction of citric acid with hydriodic acid; (6) from propane-*ααβγγ*-pentacarboxylic ester (see this), by the elimination of $2CO_2$ (B. **25**, R. 746); (7) by the action of caustic potash upon citrazinamide at 150° (B. **27**, 1271, 3456). The acid occurs in unripe beets, and also in the deposit in the vacuum pans used in beet-sugar works.

The *silver salt*, $C_6H_5O_6Ag_3$. *Calcium tricarballylate*, $(C_6H_5O_6)_2Ca_3 + 4H_2O$, is a powder that dissolves with difficulty. The *trimethyl ester*, $C_6H_5O_6(CH_3)_3$, boils at 150°, under a pressure of 13 mm. The *chloride*, $C_3H_5(CO.Cl)_3$, boils at 140° (14 mm.) (B. **22**, 2921). *Anhydride acid*, $C_5H_6O_5$, melts at 131–132° (B. **24**, 2890). The *triamide*, $C_3H_5(CO.NH_2)_3$, melts at 206°. The *amidimide*, $C_6H_8O_3N_2$, melts at 173° (B. **24**, 600).

Camphoronic Acid, *ααβ-Trimethyltricarballylic Acid*,



$$\begin{array}{lllll} & CO_2H & & CO_2H & CO_2H \\ & | & & | & | \\ CH_3- & C & — & C & — CH_2, \\ & | & & | & \\ & CH_3 & & CH_3 & \end{array}$$

melting at 135°, is formed by the oxidation of camphor and will be discussed in connection with this, as its constitution has become of prime importance in explaining the structure of camphor.

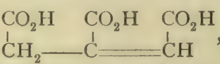
Homologous Tricarballylic Acids: *α-Methyl-* two modifications, melting at 180° and 134°; *β-Methyl-* melting at 164°; *α-Ethyl-* melting at 147–148°; *α-n-Propyl*, melting at 151–152°; *α-Isopropyl-tricarballylic Acid*, melting at 161–162° (B. **24**, 2887). *αα₁-Dimethyl-tricarballylic Acid*, three modifications; see B. **29**, 616.

αβδ-Butane Tricarboxylic Acid melts at 116–120°.

αγε-Pentane Tricarboxylic Acid melts at 106–107° (B. **24**, 284).

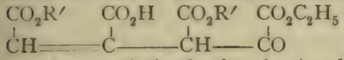
B. OLEFINE TRICARBOXYLIC ACIDS.

Aconitic Acid,



$$\begin{array}{lll} CO_2H & CO_2H & CO_2H \\ | & | & | \\ CH_2 — & C = & CH \end{array}$$

, melts at 191°, and at the same time decomposes into CO_2 and itaconic anhydride (p. 465). It is isomeric with trimethylene tricarboxylic acid (see this), and occurs in different plants; for example, in *Aconitum Napellus*, in *Equisetum fluviatile*, in sugar cane, and in beet roots. It is obtained by heating citric acid alone or with concentrated hydrochloric or sulphuric acid (B. **20**, R. 254).

Aconitic acid has been synthetically made by the decomposition with alkali of the synthetic product resulting from the union of 2 mols. of oxalic ester and 2 mols. of acetic ester,  $\overset{CO_2R'}{\overset{|}{CH}} = \overset{CO_2H}{\overset{|}{C}} - \overset{CO_2R'}{\overset{|}{CH}} - \overset{CO_2C_2H_5}{\overset{|}{CO}}$ (B. **24**, 120); as well as by the breaking-down of the body obtained from sodium malonic ester and acetylene dicarboxylic ester (J. pr. Ch. [2] **49**, 20).

Aconitic acid dissolves readily in water. Nascent hydrogen converts it into tricarballylic acid.

The *calcium salt* $(C_6H_3O_6)_2Ca_3 + 6H_2O$, dissolves with difficulty. The *trimethyl ester*, $C_6H_3O_6(CH_3)_3$, boils at 161° (14 mm.). It results from the distillation of acetyl citric trimethyl ester (B. **18**, 1954), and from aconitic acid, methyl alcohol, and hydrochloric acid (B. **21**, 669).

The *triamide*, $C_3H_3(CONH_2)_3$, is converted into citrazinic acid (see this) by acids (B. **22**, 1078, 3054; **23**, 831).

Aceconitic and **Citracetic Acids**, $C_6H_6O_6$, are two acids of unknown constitution. They are isomeric with aconitic acid. They result when sodium acts upon bromacetic ester (A. **135**, 306).

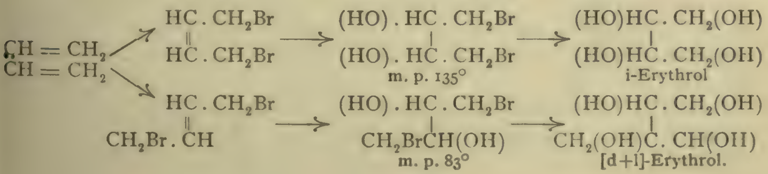
Allene Tricarboxylic Ester, $CO_2R . CH : C : C(CO_2R)_2$, from β-dibromacrylic ester and disodium malonic ester, melts at 107° (B. **29**, R. 851).

VI. TETRAHYDRIC ALCOHOLS AND THEIR OXIDATION PRODUCTS.

I. TETRAHYDRIC ALCOHOLS.

Ordinary erythrol is the best known of the tetrahydric alcohols corresponding to the four tartaric acids (p. 521). By an intramolecular compensation it, like mesotartaric acid, becomes optically inactive, and is therefore called i-erythrol. This alcohol and [d + l] erythrol were synthetically prepared by Griner in 1893 from divinyl.

Divinyl, or butadiën (p. 99), forms an unstable dibromide, which rearranges itself at 100° into two different but stable dibromides. When these are oxidized by potassium permanganate, the one passes into the dibromhydrin (melting at 135°) of ordinary or i-erythrol, while the other becomes the dibromhydrin (melting at 83°) of [d + l] erythrol. Caustic potash converts these two dibromhydrins into two butadiën oxides, which with water yield the erythrols corresponding to i- and [d + l] erythrol (B. **26**, R. 932):

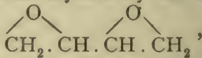


i-Erythrol, *Erythrite*, *Erythroglucin* or *Phycite*, $CH_2(OH).CH(OH).CH(OH).CH_2.OH$, occurs free in the alga *Protococcus vulgaris*. It exists as erythrin (orsellinate of erythrite) in many lichens and some algæ, especially in *Roccella Montagnei*, and is obtained from these by saponification with caustic soda or milk of lime:

$$\underset{\text{Erythrin}}{C_4H_6\begin{cases}(OH)_2\\(O.C_8H_7O_3)_2\end{cases}} + 2H_2O = \underset{\text{Erythrol}}{C_4H_6(OH)_4} + \underset{\text{Orsellinic Acid.}}{2C_8H_8O_4.}$$

Like all polyhydric alcohols erythrol possesses a sweet taste. It melts at 126° and boils at 330°.

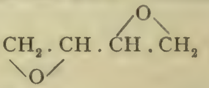
By carefully oxidizing erythrol with dilute nitric acid *erythrose* results. More intense oxidation produces erythritic acid and mesotartaric acid (p. 526).

i-Nitro-erythrol, $C_4H_6(ONO_2)_4$, melts at 61° and explodes violently when struck. **i-Tetra-acetyl Erythrol,** $C_4H_6(OCOCH_3)_4$, melts at 85°. **i-Erythrol Dichlorhydrin,** $C_4H_6(OH)_2Cl_2$, melting at 125°, is formed from erythrol by the action of concentrated hydrochloric acid. **i-Erythrol-Ether,**  $\overbrace{CH_2.CH}^{O}.\overbrace{CH.CH_2}^{O}$, boiling at 138°, with sp. gr. 1.113 (18°), is formed when caustic potash acts upon dichlorhydrin. It is a liquid with a penetrating odor, and deports itself like ethylene oxide (p. 298). It slowly combines with water, yielding erythrol, with 2HCl to the dichlorhydrin, and with 2CNH to the nitrile of dioxyadipic acid (B. **17**, 1091). Erythrol, in the presence of hydrochloric acid, combines with formaldehyde, benzaldehyde, and acetone, yielding:

i-Erythrol-formal, $C_4H_6O_4(CH_2)_2$, melting at 96° (A. **289**, 27);

i-Erythrol-dibenzal, melting at 97°; and

i-Diacetone Erythrol, $C_4H_6O_4(C_3H_6)_2$, melting at 56° and boiling at 105° (29 mm.) (B. **28**, 2531).

[d + l]-**Erythrol** melts at 72°; formation—see above. **Dibromhydrin** melts at 83° (see above); [d + l] **Erythrol Ether,**  $\underbrace{CH_2.CH}_{O}.\overbrace{CH.CH_2}^{O}$ (B. **26**, R. 933).

Tetra-acetyl [d + l] *Erythrol* melts at 53°.

Nitrotertiary Butyl Glycerol, $NO_2C(CH_2OH)_3$, melting at 158°, is formed from nitromethane, formaldehyde, and some potassium bicarbonate (B. **28**, R. 774).

Pentaerythrol, $C(CH_2OH)_4$, melting at 250–255°, has been prepared by condensing formaldehyde and acetaldehyde with lime. See also vinyltrimethylene. *Tetra-acetyl Pentaerythrol*, $C(CH_2.O.COCH_3)_4$, melts at 84° (A. **276**, 58). **Pentaerythrol Dibenzal** melts at 160° (A. **289**, 21). Two **Hexyl-erythrols** have been prepared by oxidizing diallyl, $CH_2 = CH.CH_2 — CH_2—CH = CH_2$ (p. 99).

2. **TRIOXYALDEHYDES** and 3. **TRIOXYKETONES: Erythrose,** *Tetrose*, is probably a mixture of a trioxyaldehyde and a trioxyketone (compare *glycerose*, p. 477). It is produced when erythrol is oxidized with dilute nitric acid. It yields **phenylerythrosazone,** $C_4H_6O_2(N_2HC_6H_5)_2$, melting at 167° (B. **20**, 1090). This probably is also produced from the condensation product of glycolyl aldehyde (B. **25**, 2553).

Methyl Tetrose, $CH_3[CHOH]_3CHO$, is formed from rhamnoseoxime and acetic anhydride. The *osazone*, melting at 171–174°, becomes d-tartaric acid when it is oxidized with nitric acid (B. **29**, 1381).

4. **OXYTRIKETONES:** 3-Methyl-3-heptanol-2.5.6-trion, aldol of diacetyl, $CH_3.COC(OH).CH_3.CH_2.CO.CO.CH_3$, boils at 128° (18 mm.) (p. 322).

5. **TETRAKETONES:** *Tetra-acetyl Ethane*, $(CH_3CO)_2CH - CH(CO . CH_3)_2$, is obtained from sodium acetylacetone by means of iodine or by electrolysis (p. 323).

Oxalyl Diacetone, $CH_3 . CO . CH_2 . CO . CO . CH_2 . CO . CH_3$, melting at 120–121°, is obtained by the action of sodium ethylate upon oxalic ester and acetone (B. **21**, 1142). It forms a dipyrazole derivative with phenylhydrazine (A. **278**, 294).

Methenylbisacetyl Acetone, $(CH_3CO)_2CH . CH = C(COCH_3)$, is obtained from ethoxymethylene acetyl acetone (p. 478) by the addition of acetyl acetone.

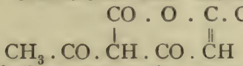
6. **TRIOXYMONOCARBOXYLIC ACIDS:**

Erythritic Acid, $C_3H_4 \left\{ \begin{matrix} (OH)_3 \\ CO_2H \end{matrix} \right.$, erythroglucic acid, trioxybutyric acid, is produced in the oxidation of erythrol, mannitol, and lævulose (B. **19**, 468). It forms a deliquescent crystalline mass.

Trioxyisobutyric Acid, $(CH_2OH)_2C(OH)CO_2H$, melting at 116°, is formed from glycerose and CNH (B. **22**, 106).

7. **DIOXYKETONE MONOCARBOXYLIC ACIDS:** *aγ-Diethoxyaceto-acetic Ester*, $CH_2(OC_2H_5) . CO . CH(O . C_2H_5)CO_2C_2H_5$, boiling at 131–132° (14 mm), results from the action of sodium ethylate upon ethoxychloracetoacetic ester (p. 482) (A. **269**, 28) (p. 477).

8. **OXYDIKETONE CARBOXYLIC ACIDS:** *Dehydracetic Acid*, (6) Methyl-(3)-acetopyronon,



$$\begin{array}{l} \qquad\qquad\quad CO\ .\ O\ .\ C . CH_3 \\ \qquad\qquad\quad |\qquad\qquad\ \ \| \\ CH_3 . CO . CH . CO . CH \end{array}$$

, melting at 108° and boiling at 269°, is formed on boiling acetoacetic ester with a return cooler, on evaporating dehydracetocarboxylic acid with caustic soda (A. **273**, 186), and from acetyl chloride by the action of pyridine. It is isomeric with isodehydracetic acid (p. 496). Feist explained its constitution (A. **257**, 261; B. **27**, R. 417). Hydriodic acid converts it into dimethyl pyrone,

$CH_3 . \overbrace{C = CH . CO . CH = C} . CH_3$

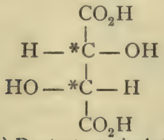
(see this).

9. **TRIKETONE-MONO-CARBOXYLIC ACIDS:** The β-phenylhydrazone formed from sodium acetone-oxalic acid and diazobenzenechloride is a derivative of *aβγ-triketo-n-valeric acid*. It melts from 206–207° (A. **278**, 285).

10. DIOXYDICARBOXYLIC ACIDS.

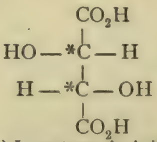
Tartaric Acids or Dioxyethylene Succinic Acids.—Tartaric acid is known in four modifications; all possess the same structure and can be converted into one another. They are: (1) *Ordinary* or *dextro-tartaric acid.* (2) *Lævo-tartaric Acid.* These two are distinguished from each other by their equally great but opposite molecular rotatory power. (3) *Racemic Acid* or *paratartaric acid*, or [d + l] tartaric acid. This is optically inactive. It can be resolved into dextro- and lævo-tartaric acids, from which it can again be recovered by their union. (4) *Mesotartaric Acid*, antitartaric acid, i-tartaric acid. This is optically inactive and cannot be split into other forms. The isomerism of these four acids was exhaustively considered in the introduction. According to the theory of van 't Hoff and Le Bel, it is attributable to the presence of two asymmetric carbon atoms in the dioxyethylene succinic acid. A compound containing one asymmetric carbon atom may occur in three modifications—a dextro-form, a lævo-form, and, by union of these two, an inactive, decomposable [d + l] modification. If the same atoms or atomic groups are joined to two asymmetric carbon atoms,—that is, if the compound be symmetrically constructed, like dioxyethylene succinic acid,—then in addition to the three modifications capable of forming a compound with one asymmetric carbon atom there arises a fourth possibility. Should, namely, the groups linked to the one asymmetric carbon atom (viewed from the point of union of the two asymmetric carbon atoms) show an opposite arrangement from that of the groups attached to the second asymmetric carbon atom, then an inactive body will result by virtue of an *intramolecular compensation.* The action on polarized light occasioned by the one asymmetric carbon atom is equalized by an equally great but oppositely directed influence exerted by the second asymmetric carbon atom.

Therefore, the four symmetrical dioxysuccinic acids can be represented by the following formulas, to which must be ascribed a spacial significance as basis (p. 48):



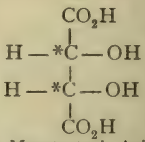
$$\begin{array}{c} CO_2H \\ | \\ H-{}^*C-OH \\ | \\ HO-{}^*C-H \\ | \\ CO_2H \end{array}$$

(1) **Dextrotartaric Acid**



$$\begin{array}{c} CO_2H \\ | \\ HO-{}^*C-H \\ | \\ H-{}^*C-OH \\ | \\ CO_2H \end{array}$$

(2) **Lævotartaric Acid**



$$\begin{array}{c} CO_2H \\ | \\ H-{}^*C-OH \\ | \\ H-{}^*C-OH \\ | \\ CO_2H \end{array}$$

(3) **Mesotartaric Acid.**

d-Tartaric acid + l-tartaric acid = (4) Racemic Acid.

The configuration of d-tartaric acid, as represented on p. 563, follows in consequence of the formation of this acid from the oxidation of methyl tetrose, the decomposition product of the rhamnoses.

Historical.—Scheele in 1769 showed how this acid could be isolated from argol. Kestner in 1822 discovered *racemic acid* as a by-product in the manufacture of ordinary tartaric acid, and in 1826 Gay-Lussac investigated the two acids. Very soon both he and Berzelius (1830) proved that ordinary tartaric acid and racemic acid possessed the same composition, and this fact led Berzelius to introduce the term *isomerism* into chemical science (p. 41). Biot (1838) showed that a solution of ordinary tartaric acid rotated the plane of polarized light to the right, whereas the solution of racemic acid proved to be optically inactive, and was without action upon the polarized ray. Pasteur's classic investigations (1848–1853) demonstrated how racemic acid could be resolved into *dextro-* and *lævo-tartaric acid*, and be again re-formed from them. In addition to lævo-tartaric acid, Pasteur also discovered inactive or *mesotartaric acid*, which cannot be resolved. Kekulé in 1861 and, independently of him, Perkin, Sr., and Duppa synthesized racemic acid and mesotartaric acid from succinic acid, derived from amber, through the ordinary dibromsuccinic acid. In 1873 Jungfleisch obtained racemic acid and mesotartaric acid from synthetic succinic acid, and also the other two tartaric acids derivable from racemic acid. Van 't Hoff in 1874 and, independently of him, Le Bel referred the isomerism of the four tartaric acids to the presence of two asymmetric carbon atoms in symmetrical dioxyethylene succinic acid.

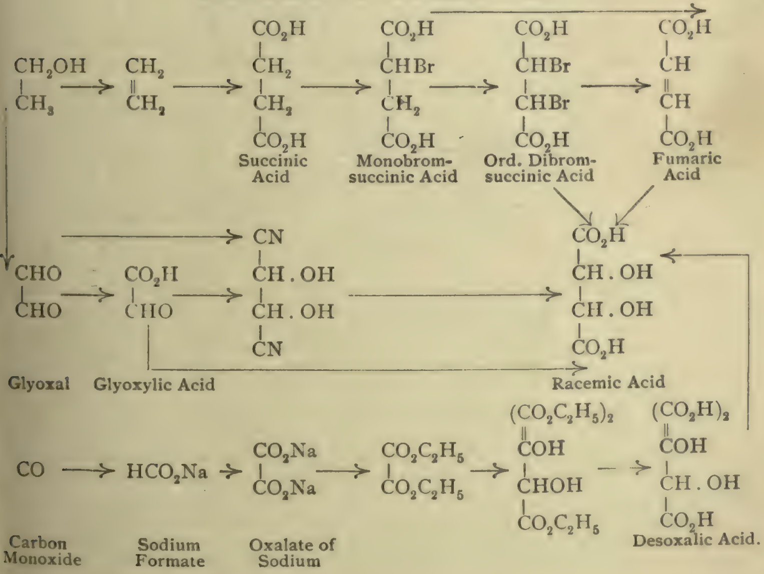
Kekulé and Anschütz in 1880 and 1881 found that when racemic acid was oxidized it yielded *fumaric acid*, and that inactive or mesotartaric acid gave maleïc acid. The oxidant was potassium permanganate. This reaction directly linked the isomerism of the tartaric acids to the isomerism of the two unsaturated acids—fumaric acid and maleïc acid.

(1) **Racemic Acid,** *Paratartaric Acid*, $C_4H_6O_4 + H_2O$, is sometimes found in conjunction with tartaric acid in the juice of the grape, and is obtained from the mother liquor in crystallizing cream of tartar, especially in the presence of alumina.

Racemic acid appears (1) in the oxidation of mannitol, dulcitol and mucic acid with nitric acid, as well as when fumaric acid (B. **13**, 2150), sorbic acid, and piperic acid are oxidized by potassium permanganate (B. **23**, 2772). It is synthetically obtained (2) from glyoxal by means of prussic and hydrochloric acids (together with mesotartaric acid, B. **27**, R. 749), and (3) from isodibrom- and (together with mesotartaric acid) from dibromsuccinic acid, by the action of silver oxide (pp. 452, 526); (4) together with glycollic acid (compare the pinacone formation, p. 293), when glyoxylic acid is reduced with acetic acid and zinc; (5) in addition, by heating desoxalic acid with water to 100°, when carbon dioxide is split off.

Ethyl alcohol, which can be synthesized in various ways, constitutes the starting-out material for the first four syntheses. In the fifth synthesis carbon monoxide serves for that purpose.

SYNTHESIS OF RACEMIC ACID.



Racemic acid is also produced when equal quantities of concentrated solutions of dextro- and lævo-tartaric acids are mixed (B. **25**, 1566), and together with mesotartaric acid when ordinary tartaric acid is heated with water to 175°.

Racemic acid crystallizes in rhombic prisms which slowly effloresce in dry air. It is less soluble (1 part in 5.8 parts at 15°) in water than the tartaric acid, and has no effect on polarized light. It loses its crystal water when heated to 110°. In the anhydrous condition it melts at 205–206°. It foams at the same time. Potassium permanganate oxidizes it to oxalic acid and hydriodic acid reduces it to inactive malic and ethylene succinic acids. Its *salts* closely resemble those of tartaric acid, but do not show hemihedral faces. The acid *potassium salt* is appreciably more soluble than cream of tartar. The *calcium salt*, $C_4H_4O_6Ca + 4H_2O$, dissolves with more difficulty than the corresponding salts of the three other tartaric acids. Acetic acid and ammonium chloride do not dissolve it. It is formed on mixing solutions of calcium dextro- and lævotartrates. *Barium salt*, $C_4H_4O_6Ba + 2\frac{1}{2}H_2O$ or $5H_2O$ (A. **292**, 311).

Decomposition of Racemic Acid.—When Pasteur was studying racemic acid he discovered methods for the decomposition of optically inactive bodies into their optically active components. These were briefly considered in the introduction (p. 68):

(1) *Penicillium glaucum* destroys the dextro-tartaric acid growing in a racemic acid solution, leaving the l-tartaric acid undisturbed.

(2*a*) From a solution of sodium ammonium racemate unaltered salt, without hemihedral faces, separates above +28° (B. **29**, R. 112). When the crystallization takes place below +28°, large rhombic crystals form. Some of these show right, others left hemihedral faces. Removing the similar forms, or by testing a solution of the crystals with a solution of calcium dextro-tartrate (A. **226**, 197), we discover that the former possess right-rotatory power and yield common tartaric acid, whereas the latter yield the lævo-acid.

(2*b*) From a solution of cinchonine racemate the first crystallization consists of the more sparingly soluble lævotartrate. If only half as much cinchonine, as is necessary for the production of the acid salt, be introduced, then two-thirds of the calculated quantity of cinchonine lævo-tartrate will separate (B. **29**, 42). Quinicine dextrotartrate is the first to crystallize from a solution of quinicine racemate.

Esters of Racemic Acid: The *dimethyl ester* melts at 85° and boils at 282°. It is produced from racemic acid, methyl alcohol, and HCl. It is obtained pure by distillation under reduced pressure. It can be made by fusing together the dimethyl ester of dextro- and lævo-tartaric acids. In vapor form the ester of racemic acid dissociates into the dimethyl ester of the dextro- and lævo-tartaric acids (B. **18**, 1397; **21**, R. 643).

Diacetyl Racemic Anhydride, $(C_2H_3O_2)_2C_4H_2O_3$, melts at 122–123° (B. **13**, 1178). *Dimethyl Diacetyl Racemic Ester*, $(C_2H_3O_2)_2C_4H_2O_4(CH_3)_2$, melting at 86°, results from the action of acetyl chloride upon the dimethyl ester, and upon evaporating the benzene solution of the dimethyl l- and d-diacetyl tartaric esters. *Nitrile of Diacetylpyroracemic Acid*, $CH_3 . CO . O . CH(CN) . CH(CN)O . COCH_3$, melting at 97°, is produced together with the nitrile of diacetyl mesotartaric acid, when acetic anhydride acts upon the liquid portion of the additive product resulting from CNH and glyoxal in alcohol (B. **27**, R. 749).

Imides: *Methyl-*, *ethyl-*, and *phenyl-imides* melt at 157°, 179°, and 235° (B. **29**, 2719). The *anil* of diacetylracemic acid melts at 94°. It results when PCl_5 acts upon the anilic acid, and when the anils of d- and l-diacetyltartaric acids combine (privately communicated by Anschütz and Reitter).

(2) **Dextro-rotatory or Ordinary Tartaric Acid** (*Acidum tartaricum*) is widely distributed in the vegetable world, and occurs principally in the juice of the grape, from which it deposits after fermentation in the form of acid potassium tartrate (argol). It results on oxidizing saccharic acid and milk sugar with nitric acid.

Common tartaric acid crystallizes in large monoclinic prisms, which dissolve readily in water (1 part in 0.76 parts at 15°) and alcohol, but not in ether. Its solution turns the ray of polarized light to the right. It melts at 167–170° (B. **22**, 1814), when rapidly heated. When it is heated with water to 165° it changes mainly to mesotartaric acid; at 175° the racemic acid predominates. It also forms racemic acid when it is brought together with a concentrated solution of l-tartaric acid. Pyroracemic and pyrotartaric acids are products of its dry distillation.

When gradually oxidized, d-tartaric acid becomes dioxyfumaric acid (p. 527), dioxytartaric acid, and tartronic acid (p. 485); stronger oxidizing agents decompose it into carbon dioxide and formic acid.

Hydriodic acid reduces it to d-malic and ethylene succinic acids.

d-Tartaric acid is applied in dyeing or coloring, as an ingredient of effervescing powders, and as a medicine. Nearly all of its salts meet with extended uses.

Tartrates.—The *neutral potassium salt*, $C_4H_4K_2O_6 + \frac{1}{2}H_2O$, is readily soluble in water; from it acids precipitate the salt $C_4H_5KO_6$, which is not very soluble in water, and constitutes natural tartar-*argol* (*Cremor tartari*). *Potassium-Sodium Tartrate*. $C_4H_4KNaO_6 + 4H_2O$ (*Seignette's salt*), crystallizes in large rhombic prisms with hemihedral faces. The *sodium-ammonium salt*, $C_4H_4KNaO_6 + 4H_2O$, is obtained from sodium-ammonium racemate. The *calcium salt*, $C_4H_4CaO_6 + H_2O$, is precipitated from solutions of neutral tartrates, by calcium chloride, as an insoluble, crystalline powder. It dissolves in acids and alkalies, and is reprecipitated as a jelly on boiling—a reaction serving to distinguish tartaric from other acids. See also calcium racemate.

The *neutral lead salt*, $C_4H_4PbO_6$, is a curdy precipitate.

Tartar Emetic.—*Potassio-antimonyl Tartrate*, $C_4H_4(SbO)KO_6 + \frac{1}{2}H_2O$, or $C_4H_4O_6 : SbOK + \frac{1}{2}H_2O$, or $CO_2K[CHOH]_2COOSb\genfrac{<}{>}{0pt}{}{O}{O}Sb . OCO[CHOH]_2 . COOK + H_2O$ (B. **16**, 2386), is prepared by boiling cream of tartar with antimony oxide and water. It crystallizes in rhombic octahedra, which slowly lose their water of crystallization on exposure and fall to a powder. It is soluble in fourteen parts of water at 10°. Its solution possesses an unpleasant metallic taste, and acts as a sudorific and emetic. See B. **29**, R. 84; **28**, R. 463, for the corresponding arsenic compound.

d-Dextro-tartaric Acid Esters (compare racemic esters). To obtain the esters of tartaric acid, $C_2H_4O_2(CO_2R)_2$, dissolve the acid in methyl or ethyl alcohol, conduct hydrochloric acid gas through the solution, and distil the liquid under diminished pressure. PCl_5 converts them into esters of chlormalic acid (p. 489) and chlorfumaric acid. The esters constitute the first homologous series of optically active substances, which were investigated along the line of rotation of the plane of polarized light (Anschütz and Pictet, B. 13, 1177; compare C. **65**, 996; B. **27**, R. 511, 621, 725, 729; B. **28**, R. 148). The *dimethyl ester* melts at 48° and boils at 280° (760 mm.), $[\alpha]_D = +2.142$ (20°). The *diethyl ester* boils at 280° (760 mm.), $[\alpha]_D = +7.659$ (20°). The *di*-n-*dipropyl ester* boils at 303° C. (760 mm.), $[\alpha]_D = +12.442$ (20°).

Diacetyl-d-tartaric Anhydride, $(C_2H_3O_2)_2C_4H_2O_3$, melts at 125–129°.

Diacetyl Dimethyl Ester melts at 103°.

Diacetyl Tartaric Dianilide melts at 214° (A. **279**, 138).

Diacetyl-d-tartranil; see the anil of diacetyl pyroracemic acid, p. 524; other imides, B. **29**, 2710.

By dissolving pulverized tartaric acid in concentrated nitric acid and adding sulphuric acid, so-called *Nitro-tartaric Acid*, $C_2H_2(O.NO_2)_2<\begin{matrix}CO_2H\\CO_2H\end{matrix}$ results. It decomposes in aqueous solution with the formation of dioxytartaric acid (p. 527). $CO_2H.C(OH)_2 — C(OH)_2CO_2H$, which further breaks down into CO_2 and tartronic acid.

(3) **Lævo-Tartaric Acid** is very similar to the dextro-variety, also melts at 167–170°, and only differs from it in deviating the ray of polarized light to the left. Their salts are very similar, and usually isomorphous, but those of the lævo-acid exhibit opposite hemihedral faces.

The dimethyl ester has the same melting and boiling points as the dimethyl ester of d-tartaric acid (see above); also compare racemic acid esters (p. 524). In the description of racemic acid the method by which l-tartaric acid could be obtained from it was exhaustively considered (p. 524). In concentrated solution it combines with d-tartaric acid and yields racemic acid.

(4) **Inactive Tartaric Acid**, *Mesotartaric Acid*, *Antitartaric Acid*, is obtained when sorbine and erythrol are oxidized with nitric acid, or (together with racemic acid) when dibromsuccinic acid is treated with silver oxide (p. 523) and maleïc acid and phenol with potassium permanganate (B. **24**, 1753). It is most readily prepared by heating common tartaric acid with water to 165° for two days. It contains a molecule of water of crystallization.

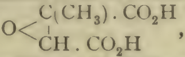
Calcium Salt, $C_4H_4O_6Ca + 3H_2O$ (A. **226**, 198). **Barium Salt**, $C_4H_4O_6 + H_2O$ (A. **292**, 315). **Dimethyl Ester** melts at 111°. **Diethyl Ester** melts at 54°, and boils at 156° (14 mm.) (B. **21**, 517). **Mesotartaronitrile**, $CN.CH(OH).CH(OH)CN$, melts with decomposition at 131°. It is produced by the addition of prussic acid to glyoxal, dissolved in alcohol. **Diacetylmesotartaronitrile** melts at 76° (B. **27**, R. 749).

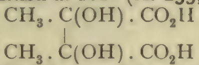
Diamidosuccinic Acids, $CO_2H.CH(NH_2).CH(NH_2).CO_2H$, are formed when the diphenylhydrazone of dioxosuccinic acid (p. 528) is reduced with sodium amalgam. The one acid corresponds to mesotartaric acid (see above), the other to racemic acid (p. 523). This has been proved by changing the amido-acids into these acids (B. **26**, 1980).

Dianilinosuccinic Ester, $CO_2C_2H_5.CH(NHC_6H_5).CH(NHC_6H_5).CO_2C_2H_5$, melting at 149°, is obtained from dibrom- and isodibrom-succinic ester and alcoholic aniline heated to 100° (B. **27**, 1604).

Imidoethylsuccinic Acid, $NH<\begin{matrix}CH.CO_2C_2H_5\\|\\CH.CO_2H\end{matrix}$, melting at 98°, is obtained by the action of hydrochloric acid upon imidosuccinamic ester, the product resulting from the action of alcoholic ammonia upon bromsuccinic ester (B. **25**, 646).

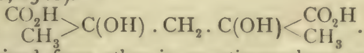
Azinsuccinic Ester, $(CO_2C_2H_5)_2 . C_2H_2 . N_2 . C_2H_2(CO_2C_2H_5)$, is obtained from diazoacetic ester; an isomeric ester is obtained from diazosuccinic ester (B. **29**, 763).

Oxycitraconic Acid,

$O<\begin{matrix} C(CH_3) . CO_2H \\ | \\ CH . CO_2H \end{matrix}$
, decomposes at 162°. It is formed when *α-chlorcitramalic acid*, melting at 139°, the addition product of ClOH and citraconic acid, is treated with caustic alkali. Hydrochloric acid changes it to *β*-chlorcitramalic acid, melting with decomposition at 162° (A. **253**, 87).

Dimethyl Racemic Acid,

$\begin{matrix} CH_3 . C(OH) . CO_2H \\ | \\ CH_3 . C(OH) . CO_2H \end{matrix}$
$+ H_2O$, is produced (1) by the reduction of pyroracemic acid (B. **25**, 397), and (2) when hydrocyanic and hydrochloric acids act upon diacetyl (p. 322). The acid melts at 177–178° (B. **22**, R. 137).

αβ-Dioxyglutaric Acid, $CO_2H . CH(OH) . CH(OH) . CH_2 . CO_2H$, melting from 155–156°, is obtained from the addition product of glutaconic acid (B. **18**, 2517).

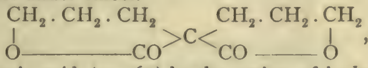
αγ-Dioxyglutaric Acid, $CO_2H . CH(OH) . CH_2 . CH(OH) . CO_2H$, is formed from dioxypropenyl tricarboxylic acid, the oxidation product of isosaccharin (p. 537) through the elimination of CO_2 (B. **18**, 2516).

αγ Dioxy-dimethyl Glutaric Acids,

$\begin{matrix} CO_2H \\ CH_3 \end{matrix}>C(OH) . CH_2 . C(OH)<\begin{matrix} CO_2H \\ CH_3 \end{matrix}$.
The acid, melting at 98°, has been obtained from ether in enantiomorphous crystals. The second acid readily changes to a *lactonic acid*, melting at 189–190°. This yields a *dilactone*, melting at 104–105° and boiling at 235°, when it is heated. These acids are produced when acetyl acetone is treated with CNH (B. **24**, 4006; compare B. **25**, 3221).

αγ-Dioxy-αβγ-trimethyl Glutaric Acid—see B. **28**, 2940.

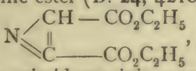
Dimethyloxyadipic Acids have been prepared from acetonyl acetone and CNH (B. **29**, 819).

Cineolic Acid, $C_{10}H_{16}O_5$, the anhydride of a dioxydicarboxylic acid resembling ethylene oxide, will be discussed later under cineol.

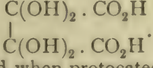
Di-ω-oxypropylmalonic Lactone,

$\begin{matrix} CH_2 . CH_2 . CH_2 \\ | \qquad\qquad | \\ O \text{———————} CO \end{matrix}>C<\begin{matrix} CH_2 . CH_2 . CH_2 \\ | \qquad\qquad | \\ CO \text{———} O \end{matrix}$
, melting at 106°, is obtained from diallylmalonic acid (p. 467) by the action of hydrobromic acid (A. **216**, 67).

Dioxyolefine Dicarboxylic Acid.—The simplest possible acid of this class appears to be formed when tartaric acid is oxidized with hydrogen peroxide in the sunlight and in the presence of a small quantity of a ferrous salt. It may be called *dioxyfumaric acid*, $CO_2H . C(OH) : C(OH) . CO_2H + 2H_2O$. *Diacetyl-dioxyfumaric acid* melts at 98° (Fenton, B. **29**, R. 547).

11. OXYKETONE DICARBOXYLIC ACIDS: *Ethoxyl-oxalo-acetic Ester*, $CO_2C_2H_5 . CO . CH(O . C_2H_5)CO_2C_2H_5$, boils at 155° (17 mm.). It is obtained from oxalic ester and ethyl glycollic ester (B. **24**, 4210).

Nitrilosuccinic Diethyl Ester,

$N\begin{matrix} \diagup CH - CO_2C_2H_5 \\ \quad \| \\ \diagdown C \text{———} CO_2C_2H_5 \end{matrix}$
, melting at 154° (40 mm.), is formed from the silver salt of *γ*-oximidosuccinic ester and ethyl iodide with subsequent distillation (B. **23**, R. 561; **24**, 2289).

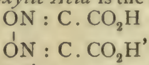
12. DIKETONE DICARBOXYLIC ACIDS.

Dioxytartaric Acid,

$\begin{matrix} C(OH)_2 . CO_2H \\ | \\ C(OH)_2 . CO_2H \end{matrix}$
. It melts with decomposition at 98° (B. **22**, 2015). It is obtained when protocatechuic acid, pyrocatechin, and guaiacol, in ethereal solution, are acted upon with N_2O_3. It was formerly regarded as carboxytartronic acid, $C(OH) . (CO_2H)_3$. Its formation from the benzene derivatives just

cited is proof for the assumption that in benzene *one* carbon atom is combined with *three* other carbon atoms. However, Kekulé removed the basis from this assumption when he showed that the body supposed to be carboxytartronic acid could also be made from nitrotartaric acid by the action of an alcoholic solution of nitrous acid, and then by reduction be converted into racemic and mesotartaric acids. He therefore named it dioxytartaric acid, for it sustains the same relation to tartaric acid that glyoxylic acid bears to glycollic acid, and mesoxalic acid to tartronic acid (A. **221**, 230). Glyoxal is formed when sodium dioxytartrate is acted upon with sodium bisulphite. The *sodium salt*, $C_4H_4Na_2O_8 + 2H_2O$, is a sparingly soluble crystalline powder.

The *dioxytartaric esters* are not known. *Dioxy-oxosuccinic Diethyl Ester*, $CO_2C_2H_5 . C(OH)_2CO . CO_2C_2H_5$, is, however, known. It consists of colorless crystals melting at 116–118°. They are produced on adding water to *dioxosuccinic diethyl ester*, $CO_2C_2H_5 . CO . CO . CO_2C_2H_5$, boiling at 232–233° (760 mm.), 115–117° (13 mm.); sp. gravity 1.1896 (20°). The distillation is conducted under reduced pressure. Hydrochloric acid acting upon sodium dioxytartaric acid suspended in alcohol produces the dioxosuccinic diethyl ester. It is a thick liquid with an orange-yellow color (B. **25**, 1975) (compare α-diketones, p. 321). When it is boiled with a return cooler CO splits off, and oxomalonic ester (p. 498) and oxalic ester result (B. **27**, 1304).

Two isomeric dioximes of dioxosuccinic acid are known (B. **24**, 1215). *Furazan Carboxylic Acid* is the oxime anhydride of the dioxime. *Dioximidohyperoxid-succinic Acid*,



$\begin{matrix} ON : C . CO_2H \\ | \\ ON : C . CO_2H \end{matrix}$, is an unstable oil, formed by oxidizing isonitroso-acetic and acetoacetic esters (p. 368) with nitric acid (B. **28**, 1213).

Dioxosuccinic acid also yields **pyrazolonopyrazolon**, a double lactazam, a monophenylhydrazone and a phenylosazone. The lactazam corresponding to the latter compound is the parent substance of a yellow dye,

Tartrazine, which will be more fully described under the pyrazolons (A. **294**, 219).

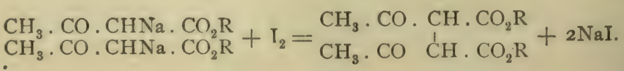
Three isomeric osazones: α-, melting at 121°; β-, melting at 136–137°; and γ-, melting at 175°, of dioxosuccinic diethyl ester are known. The α- body, when in solution, gradually changes to the β-compound. Iodine or SO_2 will accelerate the conversion. All these osazones enter the pyrazolon formation very readily.

Oxalo-diacetic Acid, *Ketipic Acid*, $CO_2H . CH_2 . CO . CO . CH_2 . CO_2H$, is precipitated in the form of a white insoluble powder on adding concentrated hydrochloric acid to the ester. It breaks down on heating into $2CO_2$ and diacetyl (p. 322).

Oxalo-diacetic Ester, Ketipic Ester, $CO_2C_2H_5 . CH_2 . CO . CO . CH_2 . CO_2C_2H_5$, is produced like oxalacetic ester (p. 499) by the action of sodium upon a mixture of oxalic ester with 2 mols. of acetic ester (B. **20**, 591); also from oxalic ester and chloracetic ester by the action of zinc (B. **20**, 202). It consists of leafy crystals melting at 77°. Ferric chloride imparts an intense red color to its alcoholic solution, chlorine and bromine convert the ester into *tetrachlor-* and *tetrabrom-oxaldiacetic ester*. The first is called *tetrachlordiketo-adipic ester*, and is also produced when chlorine acts upon dioxy-quinone dicarboxylic ester (B. **20**, 3183). The osazone of oxaldiacetic ester may be converted into *di-1-phenyl-3.3-bispyrazolon* (B. **28**, 68).

Oxal-lævulinic Ester (B. **21**, 2583).

Diacetosuccinic Acid, $C_8H_{10}O_6$. Its ethyl ester is produced by electrolysis and by the action of iodine upon sodium acetoacetic ester (A. **201**, 144; B. **28**, R. 452).

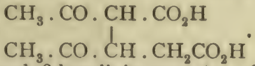


$$\begin{matrix} CH_3 . CO . CHNa . CO_2R \\ CH_3 . CO . CHNa . CO_2R \end{matrix} + I_2 = \begin{matrix} CH_3 . CO . CH . CO_2R \\ \qquad\qquad | \\ CH_3 . CO \;\; CH . CO_2R \end{matrix} + 2NaI.$$

It crystallizes in thin plates, melting at 88°. It exists also in a liquid (β-) modification, and a γ-form melting at 68° (A. **293**, 86). It is very unstable and undergoes various transformations, corresponding to its γ-diketone nature (with the atomic grouping CO . CH . CH . CO, p. 324). Thus, when heated or acted upon by acids, it yields carbopyrotritartaric ester (a derivative of furfurol). Pyrrol derivatives result when it is acted upon with ammonia and amines. This reaction will serve for the detection of diaceto-succinic ester (B. **19**, 14). Phenylhydrazone produces bispyrazolon derivatives (A. **238**, 168).

Sodium hydroxide causes the ester to break down into $2CO_2$, and acetonyl acetone (p. 324).

αβ-Diaceto-glutaric Acid,

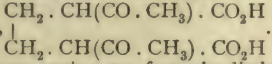


$$\begin{array}{l} CH_3.CO.CH.CO_2H \\ \quad\quad\quad\;\, | \\ CH_3.CO.CH.CH_2CO_2H \end{array}$$

. Its diethyl ester is obtained from acetoacetic ester and β-lævulinic ester (p. 381). Being a γ-diketone compound, it unites with ammonia and forms a pyrrol-derivative (B. **19**, 47).

αγ-Diaceto-glutaric Ester, $\begin{array}{l} CH_3.CO.CH — CO_2C_2H_5 \\ CH_3.CO.CH — CO_2C_2H_5 \end{array} > CH_2$, is formed from formaldehyde and acetoacetic ester in the presence of small quantities of a primary or secondary amine (Knoevenagel, A. **288**, 321). It passes readily into a tetrahydrobenzene derivative. The β-alkyl-αγ-diaceto-glutaric esters prepared from the homologous aldehydes deport themselves in a similar manner.

αδ-Diaceto-adipic Acid,

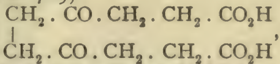


$$\begin{array}{l} CH_2.CH(CO.CH_3).CO_2H \\ | \\ CH_2.CH(CO.CH_3).CO_2H \end{array}$$

. Ethylene bromide acting upon two molecules of sodacetoacetic ester, forms its diethyl ester. Phenylhydrazine converts it into a bispyrazolon-derivative (B. **19**, 2045).

Diaceto-dimethyl Pimelic Acid (B. **24**, R. 729).

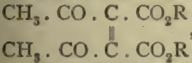
Dilævulinic Acid, 4.7-*Decandion Diacid,*



$$\begin{array}{l} CH_2.CO.CH_2.CH_2.CO_2H \\ | \\ CH_2.CO.CH_2.CH_2.CO_2H \end{array}$$

, results when alcoholic hydrochloric acid acts upon δ-furfural-lævulinic acid (A. **294**, 167).

Iodine converts disod-diaceto-succinic ester into *diaceto-fumaric ester,*



$$\begin{array}{l} CH_3.CO.C.CO_2R \\ \quad\quad\quad\; \| \\ CH_3.CO.C.CO_2R \end{array}$$

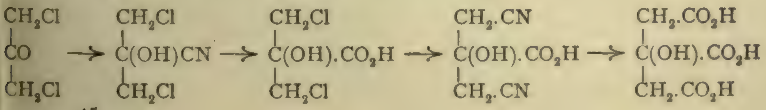
, melting at 96°.

Methenylbisacetoacetic Ester, $\begin{array}{l} CO_2C_2H_5 \\ CH_3.CO \end{array} > CH — CH = C < \begin{array}{l} CO_2C_2H_5 \\ COCH_3 \end{array}$—see ethoxymethylenacetoacetic ester (p. 483).

13. OXYTRICARBOXYLIC ACIDS.

Citric Acid, *Oxytricarballylic Acid* (*Acidum citricum*), $CO_2H.CH_2.C(OH)(CO_2H).CH_2.CO_2H + H_2O$, melts when anhydrous at 153° (B. **25**, 1159), and occurs free in lemons, in black currants, in bilberry, in beets, and in other acid fruits. It is obtained from lemon juice for commercial purposes, and also by the fermentation of glucose, induced by certain ferments: *Citromycetes pfefferianus* and *glaber* (B. **26**, R. 696; **27**, R. 78, 448).

The acid can be prepared synthetically from β-dichloracetone; this is accomplished by first acting on the latter compound with prussic acid and hydrochloric acid, when we get dichloroxyisobutyric acid, which is then treated with KCN and a cyanide obtained. The latter is saponified with hydrochloric acid:

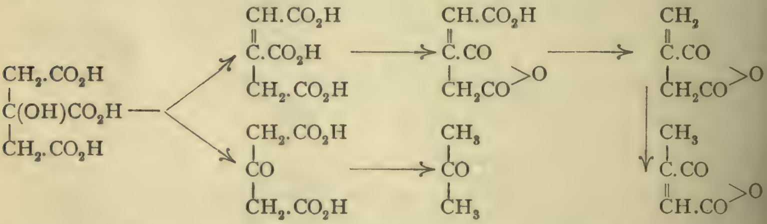


$$\begin{array}{l} CH_2Cl \\ | \\ CO \\ | \\ CH_2Cl \end{array} \rightarrow \begin{array}{l} CH_2Cl \\ | \\ C(OH)CN \\ | \\ CH_2Cl \end{array} \rightarrow \begin{array}{l} CH_2Cl \\ | \\ C(OH).CO_2H \\ | \\ CH_2Cl \end{array} \rightarrow \begin{array}{l} CH_2.CN \\ | \\ C(OH).CO_2H \\ | \\ CH_2.CN \end{array} \rightarrow \begin{array}{l} CH_2.CO_2H \\ | \\ C(OH).CO_2H \\ | \\ CH_2.CO_2H \end{array}$$

Citric acid is also obtained by the action of prussic and hydrochloric acids upon acetone dicarboxylic acid.

Properties.—Citric acid crystallizes in large rhombic prisms, which dissolve in 4 parts of water of 20°, readily in alcohol and with difficulty in ether. The aqueous solution is not precipitated by milk of lime when cold, but on boiling the tertiary calcium salt separates. This is insoluble, even in potash (see Tartaric Acid).

Transpositions.—When heated to 175° citric acid decomposes into aconitic acid (p. 518). Rapidly heated to a higher temperature aconitic acid breaks down into water and its anhydride acid, which changes to CO_2 and *itaconic anhydride*, and the latter in part to *citraconic* anhydride. Another portion of the citric acid loses water and CO_2, becoming thereby acetone dicarboxylic acid, which immediately splits into $2CO_2$ and acetone:



It breaks up into acetic and oxalic acids when fused with caustic potash, and by oxidation with nitric acid. Acetone dicarboxylic acid (p. 521) is produced when citric acid is digested with concentrated sulphuric acid.

Salts.—Being a tribasic acid it forms three series of salts, and also two different mono- and two different dialkali salts (B. **26**, R. 687).

The *calcium salt*, $(C_6H_5O_7)_2Ca_3 + 4H_2O$, is precipitated on boiling.

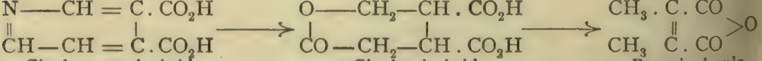
Esters: The *trimethyl ester* melts at 79° and boils at 176° (16 mm.).

Trimethyl Acetocitric Ester, boiling at 171° (15 mm.), decomposes when distilled at the ordinary pressure into acetic acid and aconitic ester (B. **18**, 1954). *Acetocitric anhydride*, melting at 121° (B. **22**, 984), breaks down when distilled at the ordinary pressure into CO_2, acetic acid and citraconic anhydride.

Citramide, $C_3H_4(OH)(CO.NH_2)_3$. When digested with hydrochloric or sulphuric acid it is condensed to *citrazinic acid* (dioxypyridine carboxylic acid) (B. **17**, 2687; **23**, 831; **27**, R. 83).

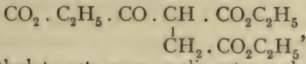
Isocitric Acid, $CO_2H.C(CH_3)(OH).CH(CO_2H).CH_2.CO_2H$, is obtained from acetosuccinic ester by means of prussic and hydrochloric acids. When liberated from its salts it immediately passes into a γ-lactone dicarboxylic acid (A. **234**, 38).

Cinchonic Acid, butenyl-δ-oxy-αβγ-tricarboxylic lactone, melting at 168° (A. **234**, 85; B. **25**, R. 904), is produced when sodium amalgam acts upon cinchomeronic acid or βγ-pyridine dicarboxylic acid. When heated to 168° it breaks down into CO_2 and pyrocinchonic anhydride (p. 466):



Cinchomeronic Acid Cinchonic Acid Pyrocinchonic Anhydride.

14. KETONE TRICARBOXYLIC ACIDS.

Oxal-succinic Ester,  $\begin{array}{l} CO_2 . C_2H_5 . CO . CH . CO_2C_2H_5 \\ \qquad\qquad\quad | \\ \qquad\qquad\; CH_2 . CO_2C_2H_5 \end{array}$, boiling at 155° (17 mm.), is formed when sodium ethylate acts upon oxalic ester and succinic ester. When it is heated alone under ordinary pressure, it breaks down into CO and ethenyl tricarboxylic ester (p. 517) (B. **27**, 797). Being a β-ketonic acid derivative, its ester yields a pyrazolon compound with phenylhydrazine. Ferric chloride imparts a red color to its alcoholic solution. It breaks down when heated above 150° into CO and ethane tricarboxylic ester (B. **27**, 797; A. **285**, 1).

a-**Acetotricarballylic Ester,** $CH_3 . CO . CH(CO_2C_2H_5)CH(CO_2C_2H_5)CH_2(CO_2C_2H_5)$, boiling at 175° (9 mm.), is obtained from chlorsuccinic ester and sodium acetoacetic ester (B. **23**, 3756).

β-**Acetotricarballylic Ester,** $CO_2 . C_2H_5 . CH_2 . C(COCH_3)(CO_2C_2H_5) . CH_2 . CO_2C_2H_5$, boiling at 190° (16 mm.), is formed from sod-acetosuccinic ester and chloracetic ester, and as a by-product in the preparation of acetosuccinic ester (A. **295**, 94); see also β-acet-glutaric acid, p. 502.

15. TETRACARBOXYLIC ACIDS.

A. PARAFFIN TETRACARBOXYLIC ACIDS.

Formation.—(1) By the action of iodine upon sodium malonic ester. (2*a*) From the sodium derivatives of malonic esters and alkylen dihalogenides or halogen malonic esters. (2*b*) From sodium tricarboxylic esters and halogen acetic esters. (3) By the addition of sodium malonic esters to the esters of unsaturated dicarboxylic acids, etc. Usually they are only known in the form of their esters.

Sym. **Ethane Tetracarboxylic Acid,** *Dimalonic Acid,* $(CO_2H)_2—CH—CH—(COOH)_2$, melts at 167–169°, and heated to higher temperatures becomes ethylene succinic acid. It is obtained from its ester by means of sodium hydroxide (B. **25**, 1158). The *ethyl ester*, melting at 76° and boiling with decomposition at 305°, is produced by electrolysis (B. **28**, R. 450); by the action of chlormalonic ester and of iodine upon sodium malonic ester, and by heating dioxalosuccinic ester (see this). Caustic potash saponifies it to ethane tricarboxylic acid with the elimination of CO_2 (p. 517). See B. **28**, 1722, for the dihydrazide.

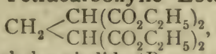
Sodium ethylate converts ethane tetracarboxylic ester into a disodium derivative, which yields tetrahydronaphthalene-tetracarboxylic ester (B. **17**, 449) with o-xylylene bromide, $C_6H_4(CH_2Br)_2$.

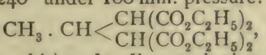
Ethyl Ethane Tetracarboxylic Ester, B. **17**, 2785.

Dimethyl Ethane Tetracarboxylic Ester, B. **18**, 1202; **28**, R. 451.

Diethyl Ethane Tetracarboxylic Ester, B. **21**, 2085; **28**, R. 452.

Alkylen Dimalonic Acids.—The following acids for practical reasons are included in this class: methylene-, ethylene-, and trimethylene-dimalonic acids. Their ethyl esters are produced when methylene iodide, ethylene bromide, and trimethylene bromide act upon sodium malonic esters.

β-**Propane Tetracarboxylic Ester,** Methylene Dimalonic Ester, Dicarboxyglutaric Ester,  $CH_2<\begin{array}{l}CH(CO_2C_2H_5)_2\\CH(CO_2C_2H_5)_2\end{array}$, is obtained by the condensation of formic aldehyde or methylene iodide (B. **22**, 3294; **27**, 2345) with two molecules of malonic ester, and by the action of zinc dust and acetic acid upon β-propylene tetracarboxylic acid (B. **23**, R. 240). It boils at 240° under 100 mm. pressure.

Ethidene Dimalonic Ester,  $CH_3 . CH<\begin{array}{l}CH(CO_2C_2H_5)_2\\CH(CO_2C_2H_5)_2\end{array}$, is produced by the union of ethidene malonic ester (see this) and sodium malonic ester.

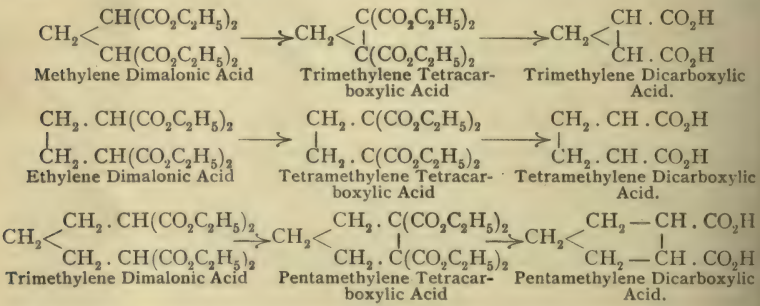
Ethylene Dimalonic Ester, Butane Tetracarboxylic Ester, $\begin{array}{l}CH_2 . CH(CO_2C_2H_5)_2\\ | \\ CH_2 . CH(CO_2C_2H_5)_2\end{array}$, is formed together with *a*-trimethylene dicarboxylic ester when ethylene bromide acts upon sodium malonic ester (B. **19**, 2038).

See, further, trimethylene-1.1-dicarboxylic acid and hexamethylene-1.1-3.3-tetracarboxylic ester.

Alkyl Butane Tetracarboxylic Ester, B. **28**, R. 300, 464.

Trimethylene Dimalonic Ester, Pentane - Tetracarboxylic Acid, $CH_2<\begin{array}{l}CH_2 . CH(CO_2C_2H_5)_2\\ CH_2 . CH(CO_2C_2H_5)_2\end{array}$, is formed, together with tetramethylene dicarboxylic ester (see this) in the action of trimethylene bromide upon two molecules of sodium malonic ester. See also hexamethylene-1.1-3.3-tetracarboxylic ester.

It is noteworthy that the disodium derivatives of the alkylen dimalonic esters are converted by the action of bromine or iodine, or of CH_2I_2 and $CH_2Br . CH_2Br$, into cycloparaffin tetracarboxylic esters. The alkylen dimalonic acids split off two CO_2 groups and yield alkylen diacetic acids; so, too, the cycloparaffin tetracarboxylic acids, obtained from the alkylen dimalonic acids, yield cycloparaffin dicarboxylic acids:



$$CH_2<\begin{array}{l}CH(CO_2C_2H_5)_2\\ CH(CO_2C_2H_5)_2\end{array} \longrightarrow CH_2<\begin{array}{l}C(CO_2C_2H_5)_2\\ | \\ C(CO_2C_2H_5)_2\end{array} \longrightarrow CH_2<\begin{array}{l}CH . CO_2H\\ | \\ CH . CO_2H\end{array}$$

Methylene Dimalonic Acid — Trimethylene Tetracarboxylic Acid — Trimethylene Dicarboxylic Acid.

$$\begin{array}{l}CH_2 . CH(CO_2C_2H_5)_2\\ | \\ CH_2 . CH(CO_2C_2H_5)_2\end{array} \longrightarrow \begin{array}{l}CH_2 . C(CO_2C_2H_5)_2\\ | \\ CH_2 . C(CO_2C_2H_5)_2\end{array} \longrightarrow \begin{array}{l}CH_2 . CH . CO_2H\\ | \\ CH_2 . CH . CO_2H\end{array}$$

Ethylene Dimalonic Acid — Tetramethylene Tetracarboxylic Acid — Tetramethylene Dicarboxylic Acid.

$$CH_2<\begin{array}{l}CH_2 . CH(CO_2C_2H_5)_2\\ CH_2 . CH(CO_2C_2H_5)_2\end{array} \longrightarrow CH_2<\begin{array}{l}CH_2 . C(CO_2C_2H_5)_2\\ \quad\quad\ | \\ CH_2 . C(CO_2C_2H_5)_2\end{array} \longrightarrow CH_2<\begin{array}{l}CH_2 - CH . CO_2H\\ \quad\quad\quad | \\ CH_2 - CH . CO_2H\end{array}$$

Trimethylene Dimalonic Acid — Pentamethylene Tetracarboxylic Acid — Pentamethylene Dicarboxylic Acid.

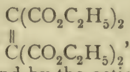
Sodium and ethyl chloracetate change ethenyl tricarboxylic ester into the ester of **Propane-*aββγ*-tetracarboxylic Acid,** $C(CO_2H)_2<\begin{array}{l}CH_2 . CO_2H\\ CH_2 . CO_2H\end{array}$, Malondiacetic acid, which boils with slight decomposition at 295° (200 mm.). The free acid is obtained by saponifying the ester. It melts at 151° and decomposes into carbon dioxide and tricarballylic acid.

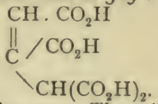
Tetracarboxylic acids are formed by the addition of sodium malonic and sodium alkyl-malonic esters to the olefine dicarboxylic esters. These acids lose CO_2 and become tricarballylic acids (p. 517) (J. pr. Ch. [2], **35**, 349; B. **24**, 311; **24**, 2889; **26**, 364).

Propane-*aaβγ*-tetracarboxylic Ester, $(CO_2C_2H_5)_2CH . CH(CO_2C_2H_5) . CH_2 CO_2C_2H_5$, boiling at 203–204°, is obtained (1) from fumaric ester and sod-malonic ester (compare ethidene dimalonic ester); (2) from monochlorsuccinic ester and sodium malonic ester (B. **23**, 3756; **24**, 596). Tricarballylic acid is produced when the ester is saponified with alcoholic potash.

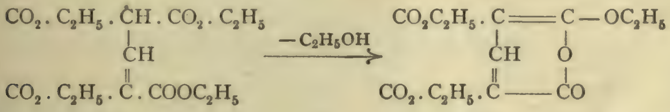
Butane-*aβγδ*-tetracarboxylic Acid, $CH_2(CO_2H)CH(CO_2H)CH(CO_2H)CH_2 . (CO_2H)$, melting at 244°, is prepared from *a*-malon-tricarballylic acid. Its *dianhydride* melts at 173° (B. **26**, 364; **28**, 882).

B. UNSATURATED TETRACARBOXYLIC ACIDS.

Ethylene or **Dicarbon-Tetracarboxylic Ester,**  $\begin{array}{c}C(CO_2C_2H_5)_2\\ \|\\ C(CO_2C_2H_5)_2\end{array}$, is obtained by letting sodium ethylate act upon chlormalonic ester, and by the action of iodine upon disodium malonic ester (B. **29**, 1290). It melts at 58°, and boils at 325°.

Propylene-*ααβγ*-tetracarboxylic Acid, $C_7H_6O_8 =$  $\begin{array}{l}CH\,.\,CO_2H\\ \|\\ C\begin{array}{l}/CO_2H\\ \backslash CH(CO_2H)_2.\end{array}\end{array}$ Its ethyl ester is formed from brommaleïc ester and sodium malonic ester. The acid contains two molecules of water of crystallization. These escape at 100°. The anhydrous acid melts at 191°, with decomposition into CO_2 and pseudo-aconitic acid melting at 145–150°.

Propylene-*ααγγ*-tetracarboxylic Ester, $CH(CO_2H)_2\,.\,CH:C(CO_2C_2H_5)_2$, dicarboxyl-glutaconic ester, results from the interaction of sodium malonic ester and chloroform. See also ethoxymethylene malonic ester (p. 494). When saponified with hydrochloric acid it yields glutaconic acid. Sodium amalgam converts it into dicarboxyl-glutaric ester. It splits off alcohol and then condenses to *δ-lactone*, melting at 93° (B. **22**, 1419; **26**, R. 9):



$$\begin{array}{c}CO_2\,.\,C_2H_5\,.\,\overset{}{C}H\,.\,CO_2\,.\,C_2H_5\\ |\\ CH\\ \|\\ CO_2\,.\,C_2H_5\,.\,C\,.\,COOC_2H_5\end{array} \xrightarrow{-C_2H_5OH} \begin{array}{c}CO_2C_2H_5\,.\,C=\!=\!=C-OC_2H_5\\ |\qquad\quad |\\ CH\qquad O\\ \|\qquad\quad |\\ CO_2\,.\,C_2H_5\,.\,C\text{——}CO\end{array}$$

When it is heated with caustic potash it decomposes into formic and malonic acids. Glutaconic acid is also produced (p. 467) (B. **27**, 3061; C. 1897, I, 29, 229). When amidines, hydrazine, and hydroxylamine act upon it, malonic ester splits off, and cyclic derivatives of oxymethylene malonic acid result (p. 494).

Allene Tetracarboxylic Ester, $(CO_2C_2H_5)_2\,.\,C:C:C(CO_2C_2H_5)_2$, from disodium- and dichlormalonic esters, melts at 94° (B. **27**, 3374).

VII. THE PENTAHYDRIC ALCOHOLS OR PENTITES AND THEIR OXIDATION PRODUCTS.

1. PENTAHYDRIC ALCOHOLS, PENTITES.

One of these occurs in nature; all the rest have been obtained by the reduction of the corresponding aldopentoses with sodium amalgam. Their constitution follows from that of the aldopentoses from which they have been prepared. The simplest pentite, $C_5H_7(OH)_5 = CH_2$-$OH\,.\,\overset{*}{C}H(OH)\,.\,CH(OH)\,.\,\overset{*}{C}HOH\,.\,CH_2OH$, can have five theoretical modifications, because in the formula two asymmetric carbon atoms are present, and they are separated by a non-asymmetric carbon atom. There are two optically active modifications, one of which is known as l-arabite. There is also an inactive modification, produced by the union of the preceding forms, and which can be split into them. Finally, there exist two optically inactive modifications due to an intramolecular compensation.

These can not be resolved. They are *xylite* and *adonite.* The pentites are oxidized to pentoses by bromine and soda (B. **27**, 2486). Compare p. 562 for the stereochemical constitution of the pentites.

1. l-**Arabite,** $C_5H_7(OH)_5$, melting at 102°, is lævorotatory after the addition of borax to its aqueous solution. It is produced by the reduction of ordinary or l-arabinose (p. 536), and has a sweet taste (B. **24**, 538, 1839 Anm.). *Benzalarabite* melts at 150° (B. **27**, 1535). *Diacetone Arabite* boils at 145–152° (23 mm.) (B. **28**, 2533).

2. **Xylite,** $C_5H_7(OH)_5$, is syrup-like and optically inactive. It results from the reduction of xylose (p. 536, B. **24**, 538; 1839 Anm.; R. 567; **27**, 2487).

3. **Adonite,** $C_5H_7(OH)_5$, melts at 102° and is optically inactive. It occurs in *Adonis vernalis*, and is produced by the reduction of ribose (p. 536; B. **26**, 633).

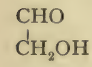
Adonit-diformacetal melts at 145° (B. **27**, 1893).

Adonit-diacetone boils at 150–155° (17 mm.).

4. **Rhamnite,** $CH_3 . C_5H_6(OH)_5$, melting at 121° and dextrorotatory, results from the reduction of rhamnose (p. 536; B. **23**, 3103).

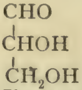
2. TETRAOXYALDEHYDES, ALDOPENTOSES.

The tetraoxyaldehydes, the first oxidation products of the pentahydric alcohols, are closely related to the pentaoxyaldehydes or aldohexoses, the first class of the carbohydrates in the more restricted sense, to which also the aldopentoses are very similar in chemical deportment. Whereas formerly the carbohydrates occupied a special position in the province of aliphatic chemistry, they are now found to be very closely allied to simpler classes of bodies. All aldehyde- and ketone-alcohols, which can be regarded as the first oxidation products of the simplest representatives of the polyhydric alcohols, contain, like the carbohydrates in a narrower sense, not only carbon, but also hydrogen and oxygen in the same proportion as water, *e. g.:*



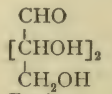
$$\begin{array}{l}CHO\\ |\\ CH_2OH\end{array}$$

Glycolyl Aldehyde (Diose, $C_2H_4O_2$)



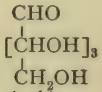
$$\begin{array}{l}CHO\\ |\\ CHOH\\ |\\ CH_2OH\end{array}$$

Glycerose (Triose, $C_3H_6O_3$)



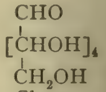
$$\begin{array}{l}CHO\\ |\\ [CHOH]_2\\ |\\ CH_2OH\end{array}$$

Erythrose (Tetrose, $C_4H_8O_4$)



$$\begin{array}{l}CHO\\ |\\ [CHOH]_3\\ |\\ CH_2OH\end{array}$$

Arabinose (Pentose, $C_5H_{10}O_5$)



$$\begin{array}{l}CHO\\ |\\ [CHOH]_4\\ |\\ CH_2OH\end{array}$$

Glucose (Hexose, $C_6H_{12}O_6$)

The simplest carbohydrates are, therefore, aldehyde-alcohols, such as those just mentioned, or ketone alcohols—*e. g.*, fructose, CH_2OH.-$CO . [CH . OH]_3CH_2 . OH$ (p. 551). The aldopentoses show the following reactions in common with the aldohexoses:

1. They form ethers with alcohols in the presence of small quantities of hydrochloric acid (B. **28**, 1156).

1*a*. They form mercaptals with the mercaptans in the presence of hydrochloric acid (B. **29**, 547).

2. They are reduced by sodium amalgam to alcohols: *pentites.*

3. Nitric acid oxidizes them to oxycarboxylic acids: *tetraoxymono-* and *trioxydicarboxylic acids*.

4. They yield osamines with methyl alcoholic ammonia (B. **28**, 3082).

5. Hydrazine converts the pentoses into *aldazines* (B. **29**, 2308).

6. Phenylhydrazine changes them to hydrazones and characteristic dihydrazones: *osazones*.

7. They yield oximes with hydroxylamine.

8. By successive treatment with prussic acid and hydrochloric acid they pass into pentaoxyacids, the lactones of which may be reduced to hexoses (p. 564), whereby consequently the synthesis of a hexose from a corresponding pentose is realized.

9. They reduce Fehling's solution.

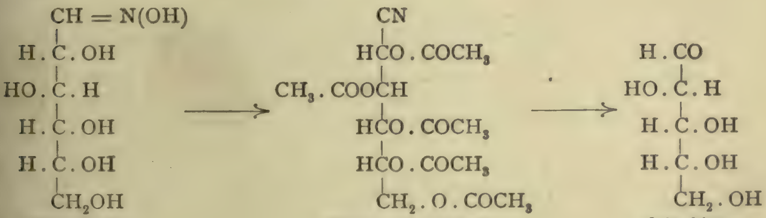
10. They combine with aldehydes, particularly with chloral and bromal.

11. They unite with acetone in the presence of traces of hydrochloric acid.

However, the aldopentoses are (1) not fermented by yeast; (2) they yield furfurol or alkyl furfurols when they are distilled with hydrochloric acid or with dilute sulphuric acid. This reaction can be applied in the quantitative determination of the aldopentoses (B. **25**, 2912). (3) When they are heated with phloroglucin and hydrochloric acid they acquire a cherry-red color (B. **29**, 1202).

Formation.—Their production from natural products will be indicated under the individual aldopentoses. However, a reaction will be given in this connection, which promises to afford a general method for the conversion of aldohexoses into aldopentoses.

On treating d-glucosoxime (p. 550) with acetic anhydride and sodium acetate, the nitrile of pentacetylgluconic acid is obtained. When this is treated with caustic alkali, and then with hydrochloric acid, it gives off first the prussic acid, and then the acetyl groups, in order to become d-arabinose (Wohl, B. **26**, 740):



$$\begin{array}{ccccc}
CH = N(OH) & & CN & & \\
H.C.OH & & HCO.COCH_3 & & H.CO \\
HO.C.H & & CH_3.COOCH & & HO.C.H \\
H.C.OH & \longrightarrow & HCO.COCH_3 & \longrightarrow & H.C.OH \\
H.C.OH & & HCO.COCH_3 & & H.C.OH \\
CH_2OH & & CH_2.O.COCH_3 & & CH_2.OH
\end{array}$$

d-Glucosoxime — Nitrile of Pentacetyl Gluconic Acid — d-Arabinose.

d-Arabinose is the first aldopentose prepared synthetically, as d-glucose (p. 553) can be synthesized.

The aldopentoses of the formula $CH_2(OH).\overset{*}{C}H.(OH).\overset{*}{C}H(OH).\overset{*}{C}H.OH.$-

CHO, containing three asymmetric carbon atoms, can appear theoretically in eight optically active isomerides, and four optically active, racemic or [d + l] modifications which can be resolved (p. 556).

1. **Arabinose**, $CH_2(OH) . (CH . OH)_3 . CHO$, is known in three modifications: l-*Arabinose*, pectinose, melting at 160°, is obtained from cherry gum on boiling with dilute sulphuric acid. Sodium amalgam converts it into arabite.

It is dextro-rotatory, and reduces Fehling's solution. Oxidation converts it into l-arabonic acid (p. 537), and l-trioxyglutaric acid (melting at 127°). Boiling hydrochloric acid converts it into furfurol.

Methyl-l-arabinoside, $C_5H_9O_5 . CH_3$, melts at 169–171° (B. **26**, 2407; **28**, 1156). l-*Arabinosazone*, $C_5H_8O_3(N_2HC_6H_5)_2$ (B. **24**, 1840 Anm.), melts at 160°. l-*Arabinose-p-bromphenylhydrazone* melts at 150–155° (B. **27**, 2490). l-*Arabinose-oxime* melts at 132–133° (B. **26**, 743). *Arabinosone*, see B. **24**, 1840 Anm. *Arabinose Ethyl Mercaptal* melts at 125°. *Arabinose Ethylene Mercaptal* melts at 154°. *Arabinose Methylene Mercaptal* melts at 150° (B. **29**, 547). *Arabinochloral*: α-form melts at 124°, the β-variety at 183°. *Arabinobromal*, $C_5H_8O_5 : CH . CBr_3$, melts at 210° (B. **29**, R. 544). *Arabinose Diacetone* melts at 42° (B. **28**, 1164).

d-*Arabinose* is formed by the breaking-down of d-glucosoxime; it is lævorotatory. d-*Arabinosazone* melts at 160°. d-*Arabinose-diacetamide*, $C_5H_{10}O_4(NH . CO . CH_3)_2$, melts at 187°.

[d + l] *Arabinose* is formed by the union of the two optically active arabinoses. [d + l]-*Arabinosazone* melts at 166° (B. **27**, 2491).

2. **Xylose**, Wood Sugar, $C_4H_5(OH)_4 . CHO$, is obtained by boiling wood-gum (beech-wood, jute, etc.) with dilute acids (B. **22**, 1046; **23**, R. 15; **24**, 1657). It is dextro-rotatory. By reduction it forms xylite (p. 534) and when oxidized, xylonic acid (p. 537) and i-trioxyglutaric acid (m. p. 152°). Prussic acid converts it into l-gulonic acid (p. 566) and l-idonic acid (p. 567).

Xylosazone melts at 160°. [d + l] *Xylosazone* melts with decomposition at 210°–215° (B. **27**, 2488). *Methyl Xyloside*, $C_5H_9O_5 . CH_3$. The α-form melts at 91°, and the β-variety at 156° (B. **28**, 1157). *Xylochloral* melts at 132° (B. **28**, R. 148).

3. **Lyxose** is formed by the reduction of the lactone of lyxonic acid (p. 537). Prussic acid converts it into acids, which yield mucic acid on oxidation (B. **29**, 584).

4. **Ribose**, $C_4H_5(OH)_4 . CHO$, is obtained from l-arabinose, by oxidizing the latter to l-arabonic acid (p. 537), then rearranging the latter to ribonic acid (p. 537) by heating it with pyridine, and finally reducing the ribonic acid (B. **24**, 4220).

5. **Rhamnose**, or **Isodulcite**, $CH_3(CH . OH)_4CHO + H_2O$, melts at 93° in anhydrous form; at 122–126° when crystallized from acetone. It is dextrorotatory (B. **29**, R. 117, 340). It results upon decomposing different glucosides (quercitrine, xanthorhamnine, hesperidine) with dilute sulphuric acid. Isodulcite yields α-methylfurfurol when distilled with sulphuric acid (B. **22**, R. 751).

It yields rhamnite upon reduction, and by oxidation l-trioxyglutaric acid (m. p. 127°). CNH and hydrochloric acid convert it into rhamnose carboxylic acid (p. 567; B. **22**, 1702). Its *oxime* has been decomposed into methyl tetrose (p. 521) (B. **29**, 1378). Its *hydrazone* melts at 159° and its *osazone* at 180° (B. **20**, 2574). *Acetone Rhamnoside*, $C_6H_{10}O_5 : C_3H_6$, melts at 90° (B. **28**, 1162). *Rhamnose Ethyl Mercaptal* melts at 136°. *Ethylene Mercaptal* melts at 169° (B. **29**, 547).

6. **Isorhamnose** has been obtained by the reduction of the lactone of isorhamnonic acid.

7. **Chinovose**, $CH_3[CH . OH]_4CHO$, isomeric with rhamnose, is a product obtained by decomposing chinovine, occurring in varieties of quina and cinchona with hydrochloric acid. Its *osazone* melts at 193–194° (B. **26**, 2417).

8. **Fucose**, $C_6H_{12}O_5$, isomeric with rhamnose, results when sea weeds (fucus varieties) are heated with dilute sulphuric acid.

3. TETRAOXYMONOCARBOXYLIC ACIDS.

Acids of this class are obtained by oxidizing the aldopentoses with bromine water or dilute nitric acid. They readily pass into lactones, some of which yield pentoses on reduction. Furthermore, oxidation changes them in part to dicarboxylic acids. Hydriodic acid reduces some of them to lactones of the monoxyparaffin carboxylic acids. All the known acids are optically active.

Tetraoxy-n-valeric acids, as aldopentoses with an equal number of carbon atoms, have theoretically eight optically active forms, three of which are known, and four [d + l] modifications.

1. **l-Arabonic Acid,** $CH_2(OH).(CH.OH)_3.CO_2H$, is obtained from l-arabinose (B. **21**, 3007). When liberated from its salts by mineral acids, it splits off water and becomes the lactone $C_5H_8O_5$, melting at 95–98°. Further oxidation changes it to trioxyglutaric acid. Its *phenylhydrazide* melts at 215° (B. **23**, 2627; **24**, 4219). When it is heated to 145° with pyridine it yields along with pyromucic acid some of the isomeric—

2. **Ribonic Acid,** which under like treatment reverts in part to arabonic acid. Its *lactone*, $C_5H_8O_5$, melts at 72–76° (B. **24**, 4217). Its *phenylhydrazide* melts at 162–164°. Arabonic and ribonic acids are lævorotatory.

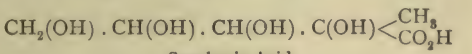
3. **Xylonic Acid,** obtained from xylose by bromine, when heated with pyridine yields—

4. **Lyxonic Acid,** the lactone of which melts at 113° (B. **29**, 581). See further lyxose, p. 536.

5. **Rhamnonic Acid,** from rhamnose and bromine, immediately passes into its lactone, $C_6H_{10}O_5$, melting at 150–151° (B. **23**, 2992; A. **271**, 73). When heated to 150° with pyridine it changes partly to—

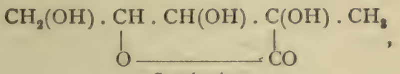
6. **Isorhamnonic Acid,** the lactone of which melts at 150–152°, and when oxidized yields xylotrioxyglutaric acid (B. **29**, 1961). See also isorhamnose, p. 536.

7. **Saccharic Acid** changes into **Saccharin,** its lactone:



$$CH_2(OH).CH(OH).CH(OH).C(OH)<\begin{matrix}CH_3\\CO_2H\end{matrix}$$

Saccharic Acid



$$\begin{array}{l}CH_2(OH).CH.CH(OH).C(OH).CH_3\\ \qquad\qquad\;\; | \qquad\qquad\quad\; | \\ \qquad\qquad\; O \text{———————} CO\end{array},$$

Saccharin

which is obtained by boiling dextrose and lævulose (or from invert sugar) with milk of lime (B. **15**, 2954). *Saccharin* dissolves with difficulty in water (in 18 parts), forms large crystals, tastes bitter, melts at 160°, and sublimes without decomposition. It is reduced to α-methyl-γ-valerolactone, or $\alpha\gamma$-dimethyl butyrolactone when heated with hydriodic acid (A. **218**, 373).

It yields a phenylhydrazide with phenylhydrazine. It melts at 165°.

Isomerides of saccharin:

Isosaccharin, $C_6H_{10}O_5$, melting at 95°, when heated with HI yields $\alpha\gamma$-dimethylvalerolactone.

Metasaccharin, $C_6H_{10}O_5$, melts at 142°. Hydriodic acid reduces it to γ-n-caprolactone (p. 346).

Both isomerides are produced when milk sugar is treated with lime (B. **18**, 631, 2514; **26**, 1651).

4. TRIOXYDICARBOXYLIC ACIDS.

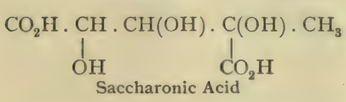
Tri-oxy-n-glutaric Acids, $CO_2H[CHOH]_3CO_2H$, can theoretically exist in four stereochemical modifications, corresponding to the four pentites (p. 533), and in addition in an inactive form, which can be decomposed.

l-Trioxyglutaric Acid, melting at 127°, corresponds to arabinose, and is formed when arabinose, sorbinose, and rhamnose are oxidized with nitric acid (B. **24**, 4214; **27**, 383; **21**, 3276).

Xylotrioxyglutaric Acid, melting at 152°, is produced by the oxidation of inactive xylose and corresponds to xylite (p. 534).

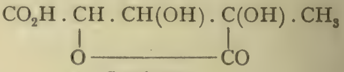
Ribotrioxyglutaric Acid, resulting from the oxidation of ribose, inactive, readily passes into an inactive *lactonic acid*, $C_5H_6O_6$, melting at 170–171° (B. **24**, 4222). It corresponds to adonite (p. 534).

Saccharon, $C_6H_8O_6$, is the lactone of **Saccharonic Acid:**



$$\underset{\displaystyle OH}{CO_2H . \underset{|}{CH}} . CH(OH) . \underset{\displaystyle CO_2H}{\underset{|}{C(OH)}} . CH_3$$

Saccharonic Acid



Saccharon.

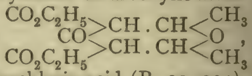
Both are formed when saccharin is oxidized by nitric acid (A. **218**, 363).

The acid is quite soluble in water. It forms large crystals. In the desiccator or when heated to 90° it breaks up into water and its l-lactone, saccharon, melting at 145–156° (A. 218, 363). On boiling with HI it is reduced to a-methyl glutaric acid (p. 453).

Trioxyadipic Acid, $C_4H_5(OH)_3<\begin{matrix}CO_2H\\CO_2H\end{matrix}$, results from the oxidation of metasaccharin (see above) with dilute HNO_3 (B. 18, 1555). It melts at 146° with decomposition. Heated with HI it is reduced to adipic acid.

5. **DIOXYKETONE DICARBOXYLIC ACIDS:** The pyrone dicarboxylic esters, resulting from the condensation of acetone dicarboxylic esters with aldehydes, are anhydrides (like ethylene oxide) of the dioxyketone dicarboxylic acids.

Dimethyl-tetrahydropyrone Dicarboxylic Ester,



$$\begin{matrix}CO_2C_2H_5>CH . CH<CH_3\\CO\lessgtr \qquad\qquad O\\CO_2C_2H_5>CH . CH<CH_3\end{matrix},$$

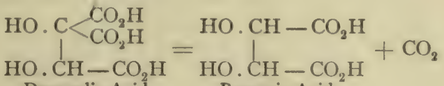
from acetone dicarboxylic ester, acetaldehyde, and hydrochloric acid (B. **29**, 994), melts at 102°.

6. **TRIKETONE DICARBOXYLIC ACIDS.** *Acetone Dioxalester*, Diethyl Xanthochelidonic Ester, $CO[CH_2 . CO . CO_2C_2H_5]_2$, melting at 103–104°, is obtained from acetone, oxalic ester, and sodium ethylate. Hydrochloric acid converts it into *Chelidonic Ester*, $CO<\begin{matrix}CH = C—CO_2C_2H_5\\CH = C—CO_2C_2H_5\end{matrix}>O$, melting at 63°. Some other acids, related to the preceding, can also be derived from *pyrone*, $CO<\begin{matrix}CH = CH\\CH = CH\end{matrix}>O$.

7. DIOXYTRICARBOXYLIC ACIDS.

TRIBASIC ACIDS.

Desoxalic Acid, $C_2H(OH)_2(CO_2H)_3$, is a deliquescent, crystalline mass. Its *tri-ethyl ester*, $C_5H_3(C_2H_5)_3O_8$, results from the action of sodium amalgam upon diethyl oxalate. It melts at 78° and boils at 156° (2 mm.). When its aqueous solution is evaporated, or when its ester is heated with water or dilute acids to 100°, the acid yields carbon dioxide and racemic acid:



$$\begin{array}{l} HO.C\lt\begin{matrix}CO_2H\\CO_2H\end{matrix} \\ \quad | \\ HO.CH-CO_2H \end{array} = \begin{array}{l} HO.CH-CO_2H \\ \quad | \\ HO.CH-CO_2H \end{array} + CO_2$$

Desoxalic Acid Racemic Acid.

Acid radicals can be substituted for the two hydroxyl groups of the desoxalic ester Heated with hydriodic acid, desoxalic acid gives off carbon dioxide, and is reduced to succinic acid.

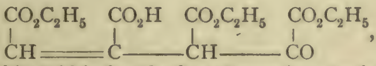
Desoxalic ester and phenylhydrazine yield phenylhydrazine glyoxylic ester, while isonitrosomalonic ester and glycollic acid are the products with hydroxylamine (B. **29**, R. 908).

Oxycitric Acid, $C_6H_8O_8 = C_3H_3(OH)_2 . (CO_2H)_3$, dioxytricarballylic acid, accompanies aconitic, tricarballylic, and citric acids in beet juice, and is produced by boiling chlorcitric acid (from aconitic acid and ClOH) with alkalies or water (B. **16**, 1078).

Dioxypropenyl Tricarboxylic Acid, $C_6H_8O_8 = C_3H_3(OH)_2(CO_2H)_3$, results from the oxidation of isosaccharin with nitric acid. It is a thick syrup. At 100° it loses carbon dioxide, and forms dioxyglutaric acid, $C_3H_4(OH)_2 . (CO_2H)_2$, which is different from the dioxyglutaric acid obtained from glutaconic acid (B. **18**, 2514). Hydriodic acid and phosphorus convert it into glutaric acid, $C_3H_6(CO_2H)_2$.

8. MONOKETONE TETRACARBOXYLIC ACIDS.

Aconitoxalic Ester,



$$\begin{array}{ccccccc} CO_2C_2H_5 & & CO_2H & & CO_2C_2H_5 & & CO_2C_2H_5 \\ | & & | & & | & & | \\ CH & = & C & - & CH & - & CO \end{array}$$

, compare p. 518.

The ammonium salt of this acid is found when ammonium oxalacetic ester is boiled with alcohol (B. **28**, 790).

9. PENTACARBOXYLIC ACIDS.

Propenyl Pentacarboxylic Acid, $C_3H_3(CO_2H_5)$, melts at 149–150°. It is obtained from its ethyl ester, which is formed by the action of sodium malonic ester upon chlorethenyl tricarboxylic ester (p. 517).

Butane Pentacarboxylic Ester, $CO_2C_2H_5 . CH_2 . CH(CO_2C_2H_5)C(CO_2C_2H_5)_2 . CH_2 . CO_2 . C_2H_5$, boiling at 216–218° (16 mm.), is obtained from chlorsuccinic ester and sodium ethenyl tricarboxylic ester.

Higher Polycarboxylic Ethyl Esters have been obtained from sodium propane pentacarboxylic esters with chlormalonic esters and chlorpentane pentacarboxylic ester:

Butane Heptacarboxylic Ester, $C_4H_3(CO_2C_2H_5)_7$, boils at 280–285° (130 mm.).

Hexane Decacarboxylic Ester, $C_6H_4(CO_2C_2H_5)_{10}$, is a yellow oil.

Octan-tesserakaideca-carboxylic Ester, $C_8H_4(CO_2C_2H_5)_{14}$, the highest known carboxylic ester, is a thick oil, and results when chlorbutane heptacarboxylic ester acts upon sodium butane heptacarboxylic ester (B. **21**, 2111).

VIII. HEXA- AND POLYHYDRIC ALCOHOLS, AND THEIR OXIDATION PRODUCTS.

1 A. HEXAHYDRIC ALCOHOLS, HEXAOXYPARAFFINS, HEXITES.

The hexahydric alcohols approach the first class of sugars (p. 572)—the glucoses—very closely. They resemble them in properties. They have a very sweet taste, but they do not reduce an alkaline copper solution, and are not fermented by yeast. δ-Mannitol, δ-sorbitol, and dulcitol occur in nature. These three and certain hexites have been prepared by the reduction of the corresponding glucoses—aldo- and keto-hexoses—with sodium amalgam. Moderate oxidation converts them into glucoses. The compounds which the hexites yield with aldehydes, especially formaldehyde and benzaldehyde, in the presence of hydrochloric acid or sulphuric acid, or with acetone and hydrochloric acid, are characteristic of them (A. **289**, 20; B. **27**, 1531; **28**, 2531).

The simplest hexites with six carbon atoms contain four asymmetric carbon atoms in the molecule. According to the theory of van 't Hoff and Le Bel, 10 *simple* spacial isomeric forms are possible for such a compound.

1. **Mannitol** or **Mannite,** $CH_2OH[CH.OH]_4CH_2OH$, exists in three modifications: dextro-, lævo-, and inactive mannitol; the latter is identical with the *a-acrite* made from synthetic *a-acrose* or [d + l] *fructose*. It is the starting-out material for the synthesis of numerous derivatives of the mannite series (B. **23**, 373), and also of *grape-sugar* (p. 548) and of *fruit-sugar* (p. 551), as will be more fully explained under these bodies. The ordinary, or d-mannitol, occurs rather frequently in plants and in the manna-ash (*Fraxinus ornus*), the dried sap of which is *manna*. It is obtained from the latter by extraction with alcohol and allowing the solution to crystallize. It is produced in the mucous fermentation of the different varieties of sugar, and may be artificially prepared by the action of sodium amalgam upon d-mannose and fruit-sugar, or d-fructose (B. **17**, 227).

Mannitol crystallizes from alcohol in delicate needles, and from water in large rhombic prisms. It possesses a very sweet taste and melts at 166°. Its solution is dextro-rotatory in the presence of borax. When oxidized with care, it yields fruit-sugar (called mannitose, B. **20**, 831), and d-mannose (B. **21**, 1805). Nitric acid oxidizes mannitol to d-mannosaccharic acid (B. **24**, R. 763; p. 569), erythritic acid, and oxalic acid. Hydriodic acid converts it into hexyl iodide.

When mannitol is heated to 200° it loses water and forms the anhydrides, *Mannitan*, $C_6H_{12}O_5$, and *Mannide*, $C_6H_{10}O_4$. The latter is also obtained by distilling mannitol in a vacuum. It melts at 87° and boils at 176° (30 mm.).

Esters.—Mannitol dichlorhydrin, $C_6H_8\left\{\begin{matrix}(OH)_4\\ Cl_2\end{matrix}\right.$, is formed when mannitol is heated with concentrated hydrochloric acid. It melts at 174°. Hydrobromic acid yields the dibromhydrin, $C_6H_8\left\{\begin{matrix}(OH)_4\\ Br_2\end{matrix}\right.$, melting at 178°.

Nitro-mannite, $C_6H_8(O\,.\,NO_2)_6$, melting at 108°, is obtained by dissolving mannitol in a mixture of concentrated nitric and sulphuric acids. It crystallizes from alcohol and ether in bright needles; it melts when carefully heated and deflagrates strongly. When struck it explodes very violently. Alkalies and ammonium sulphide regenerate mannitol.

Hexacetyl-d-Mannitol, $C_6H_8(OCOCH_3)_6$, melts at 119° (B. **12**, 2059).

Hexabenzoyl Mannitol melts at 149°.

Mannitol Triformal, $C_6H_8O_6(CH_2)_6$, melts at 227° (A. **289**, 20).

Tribenzal Mannitol, $C_6H_8O_6(CH\,.\,C_6H_5)_3$, melts at 213–217° (B. **28**, 1979).

Triacetone Mannitol, $C_6H_8O_6(C_3H_6)_3$, melting at 69°, is obtained from mannitol, acetone, and a little hydrochloric acid. It has a bitter taste (B. **28**, 1168).

Lævo-mannitol, l-Mannite, is obtained by the reduction of l-mannose (from l-arabinose carboxylic acid, p. 566) in weak alkaline solution with sodium amalgam (B. **23**, 375). It is quite similar to ordinary mannite, but melts a little lower (163–164°), and in the presence of borax is lævorotatory.

Inactive Mannitol, [d + l] Mannite, is produced in a similar manner, from inactive mannose (from i-mannonic acid). It is identical with the synthetically prepared *a*-acrite (from *a-acrose*, p. 552) (B. **23**, 383). It resembles ordinary mannitol, melts 3° higher (at 168°), and in aqueous solution is inactive even in the presence of borax. Nitric acid oxidizes it to inactive mannose and inactive mannonic acid. The latter can be resolved into d- and l-mannonic acids (B. **23**, 392). d- and l-Mannono-lactones may be reduced to d- and l-mannoses, and these to d- and l-mannites. All of these compounds have been synthesized in this way.

2. d- and l-**Idites** are colorless syrups formed by the reduction of d- and l-idoses. Their tribenzal compounds melt at 219–223° (B. **28**, 1979).

3. d-**Sorbite** (p. 558), $C_6H_{14}O_6 + H_2O$, occurs in mountain-ash berries, forming small crystals which dissolve readily in water. When heated they lose water and melt near 110°. It is produced in the reduction of d-glucose, and together with d-mannite in the reduction of d-fructose (p. 551) (B. **23**, 2623). It is reduced to secondary hexyl iodide (B. **22**, 1048) when heated with hydriodic acid.

Sorbite Triformal, $C_6H_8O_6(CH_2)_6$, melts at 206° (A. **289**, 23).

Triacetone Sorbite, $C_6H_8O_6(C_3H_6)_3$, melts at 45° and boils at 172° (25 mm.).

l-*Sorbite* (p. 558), melting at 75°, is obtained by the reduction of l-gulose (p. 551) (B. **24**, 2144).

4. **Dulcitol, Dulcite,** $C_6H_{14}O_6$, occurs in various plants, and is obtained from dulcitol manna (originating from Madagascar manna). It is made artificially by the action of sodium amalgam upon milk sugar and d-galactose. It crystallizes in large monoclinic prisms, having a sweet taste. It dissolves in water with more difficulty than mannite, and is almost insoluble in boiling alcohol. Its solution remains optically inactive even in the presence of borax (B. **25**, 2564). It melts at 188°. Hydriodic acid converts it into the same hexyl iodide that mannitol yields. Nitric acid oxidizes dulcitol to mucic acid. There is also an intermediate aldehyde compound that combines with two molecules of phenylhydrazine and forms the *osazone*, $C_6H_{10}O_4(N_2H\,.\,C_6H_5)_2$ (B. **20**, 1091).

Hexacet-dulcite melts at 171°.

Dibenzaldulcite, $C_6H_{10}O_6(CH\,.\,C_6H_5)_2$, melts at 215–220° (B **27**, 1534).

Diacetone Dulcite, $C_6H_{10}O_6(C_3H_6)_2$, melts at 98° and boils at 194° (18 mm.) (B. **28**, 2533).

5. d-*Talite* (p. 559) is a syrup. It is produced in the reduction of *a*-talose.

Tribenzal-a-talite melts at 200–206° (B. **27**, 1527).

[d + l] *Talite*, melting at 66°, is formed by the reduction of the body produced when dulcite is oxidized with PbO_2 and hydrochloric acid (B. **27**, 1530).

6. **Rhamnohexite,** $CH_3.[CH.OH]_5.CH_2OH$, melting at 173°, is formed when rhamnohexose (p. 551) is reduced with sodium amalgam (B. **23**, 3106).

1 B. **HEPTAHYDRIC ALCOHOLS: Perseïte** or **Mannoheptite,** $C_7H_9(OH)_7$, is known in three modifications: d-mannoheptite, l-mannoheptite, and [d + l] mannoheptite. The d-mannoheptite or perseïte occurs in *Laurus persea*, and is obtained, like the other two modifications, by the reduction of the corresponding mannoheptoses (B. **23**, 936, 2231). The [d + l] mannoheptite is formed when equal quantities of d- and l-mannoheptite are mixed (A. **272**, 189). Hydriodic acid reduces it to hexahydrotoluene (B. **25**, R. 503).

d- and l-Mannoheptite melt at 187°, and are optically active. [d + l] Mannoheptite melts at 203°.

a-**Glucoheptite,** $CH_2OH(CHOH)_5CH_2OH$, is obtained from *a*-glucoheptose. It melts at 127–128° (p. 553; A. **270**, 81). *Triacetone-a-glucoheptite*, $C_7H_{10}O_7(C_3H_6)_3$, boils at 200° (24 mm.) (B. **28**, 2534).

a-**Galaheptite,** $C_7H_{16}O_2$, melts at 183°. It is obtained from *a*-galaheptose (p. 553).

Anhydro-enneaheptite, $C_9H_{18}O_6$, melting at 156°, is formed from æton and formaldehyde with lime and water. It is an anhydride of the heptahydric alcohol $[CH_2OH]_3 : C.CH(OH)C : [CH_2OH]_3$ (B **27**, 1089; A. **289**, 46).

Volemite, $C_6H_2(OH)_7$, melting at 149–151°, is found in *Lactarius volemus* (B. **28**, 1973).

1 C. **OCTAHYDRIC ALCOHOLS:** *a*-**Gluco-octite,** $CH_2OH[CH.OH]_6.CH_2.OH$, is obtained from *a*-gluco-octose (p. 553, A. **270**, 98), and melts at 141°. d-**Manno-octite,** $CH_2OH[CHOH]_6CH_2OH$, from manno-octose, melts at 258°. It dissolves with difficulty in water.

1 D. **NONO-HYDRIC ALCOHOLS: Glucononite,** $C_9H_{20}O_9$, melting at 194°, is obtained from glucononose (A. **270**, 107).

2 and 3. PENTA-, HEXA-, HEPTA-, AND OCTO-OXY-ALDEHYDES AND KETONES.

The long-known representatives of the first class of carbohydrates, which are produced by hydrolysis from the more complex carbohydrates, the so-called saccharobioses (p. 573), like cane-sugar, maltose, and milk-sugar, and from the polysaccharides,—*e. g.*, starch, dextrine, cellulose, and others,—are penta-oxyaldehydes and penta-oxyketones. The most important sugar of the first class is grape-sugar, formed together with fruit-sugar by the hydrolysis of cane-sugar. It also occurs as the final product of the hydrolysis of starch and of dextrine. In this connection it may be mentioned that grape-sugar and fruit-sugar have already been noticed with ethyl alcohol, and in connection with its formation by alcoholic fermentation.

The aldehyde character of these bodies is inferred from the ready oxidation of certain glucoses to monocarboxylic acids, and their reduction to hexahydric alcohols. Zincke (1880) was the first (B. **13**, 641 Anm.) to suspect that ketone alcohols were represented among the glucoses. Kiliani, in 1885, investigating the CNH additive products, proved that grape-sugar must be regarded as an aldehyde alcohol, and fruit-sugar as a ketone alcohol. Hence it is customary to distinguish *aldoses* and *ketoses*. The same chemist also showed that arabinose was an aldopentose, and in so doing laid the basis of an extension of the idea of carbohydrates. What was lacking was a method of synthesis. It is true, sugar-like bodies had been obtained from formaldehyde (p. 552), but it was E. Fischer who first demonstrated that a definite, well-defined sugar, *a*-acrose, could be isolated from it. This, as will be observed later, became in his hands the starting-point for the synthesis of grape-sugar and of fruit-sugar.

By reducing the lactones of the polyoxycarboxylic acids to oxyaldehydes or aldoses, E. Fischer developed a method for the preparation of oxyaldehydes rich in carbon or carbohydrates from polyoxycarboxylic acids obtained synthetically from aldoses by the addition of prussic acid and subsequent saponification. In this way carbohydrates, containing seven, eight, and nine carbon atoms in the molecule, were gradually built up.

The glucoses mostly crystallize poorly, and for their isolation and recognition phenylhydrazine was used. This, E. Fischer also discovered, gave the very best assistance. Wohl showed how the oximes of the aldoses could be utilized in breaking down the same (p. 535).

The glucose character of a compound is very much affected by its constitution, as aldehyde alcohol—CH(OH) . CHO, or ketone alcohol—CO . CH_2 . OH, in which the aldehyde and ketone group is directly combined with an alcohol group or groups. We thus have glucoses containing not only *six*, but even a less or greater number of carbon and oxygen atoms. They are named according to the number of the oxygen atoms.

The simplest aldose, glycolyl aldehyde, CH_2 . OH . CHO, would be an aldodiose. Glyceric aldehyde, CH_2OH . CH . OH . CHO, and dioxyacetone, CH_2OH . CO . CH_2OH, would represent an *aldotriose* and a *ketotriose* (p. 477). The aldehyde and ketone of erythrol would be an *aldo-* and *ketotetrose*, as just developed under the pentoses (p. 534). Following the latter are the *hexoses*. In this class belong the real sugars: *grape-sugar*, *fruit-sugar*, and *galactose*. The *heptoses*, *octoses*, and *nonoses* follow in regular succession.

In addition to the long-known hexoses—grape-sugar, fruit-sugar, and galactose—many others have been discovered through E. Fischer's investigations, so that now the hexoses must be removed from the carbohydrate class, and be considered in immediate connection with their corresponding hexahydric alcohols. Then would follow the heptoses, octoses, and nonoses, as well as the oxidation products of these aldehyde and ketone alcohols: the *polyoxymonocarboxylic acids*, the *polyoxyaldehydo-carboxylic acids*, and the *polyoxypolycarboxylic acids*. After the consideration of all these, the *higher carbohydrates*, the *saccharobioses*, and the *polysaccharides*, which are the anhydrides of the hexoses, will be brought together and fully discussed (p. 572).

2 A. PENTAOXYALDEHYDES AND 3 A. PENTAOXYKETONES: HEXOSES, GLUCOSES, MONOSES.

Occurrence.—Some hexoses occur widely distributed in the free state in the vegetable kingdom, especially in ripe fruits. Esters of the glucoses (from γλύκυς, sweet) with organic acids are also frequently found in plants. They are called *glucosides*—*e.g.*, salicin, amygdalin, coniferin, the tannins, which are grape-sugar esters of the tannic acids, etc. The glucosides are split into their components by ferments, acids, or alkalies.

Formations.—(1) They are formed by the hydrolytic decomposition of all di- and poly-saccharides, as well as of glucosides, by ferments (p. 120) (B. **28**, 1429), or by boiling them with dilute acids. (2) d-Mannose and fruit-sugar or d-fructose have been made artificially by oxidizing d-mannite. (3) A far more important method pursued in the formation of the glucoses is to reduce the monocarboxylic acids (their lactones) with sodium amalgam in acid solution (E. Fischer, B. **23**, 930). (4) Different optically inactive hexoses, particularly *α-acrose* or [d + l] fructose (p. 552), have been directly synthesized by the condensation of formic aldehyde, CH_2O, and glyceric aldehyde.

E. Fischer (1890) effected the complete synthesis of grape-sugar and fruit-sugar by these methods.

Properties.—The hexoses are mostly crystalline substances, very soluble in water, but dissolving with difficulty in alcohol. They possess a sweet taste. The representatives of the hexoses occurring in nature rotate the plane of polarization, when in solution, either to the left or to the right. The image isomerides of the more important hexoses found in nature have been prepared artificially, and by the union of the corresponding dextro- and lævo-forms the optically inactive [d + l] varieties have been obtained. One of these, [d + l] fructose or *α*-acrose, has been, as previously mentioned, directly synthesized.

Transformations.—The hexoses show the common reactions of the alcohols, the aldehydes, and the ketones.

(1) The alcoholic hydrogen of the glucoses can also be replaced by metals on treating them with CaO, BaO, and PbO, forming *saccharates*, which correspond to the alcoholates, and which are again decomposed by carbon dioxide.

(2) On treating the alcoholic solutions of the hexoses with a little gaseous hydrochloric acid, their ethers result: glucosides of the alcohols (B. **26**, 2400; **29**, 2927).

(3) The hexoses combine with aldehydes, particularly with chloral, and with ketones, in the presence of inorganic acids. An exit of water occurs (B. **28**, 2496).

(4) The hydrogen of the hydroxyls can be readily replaced by acid radicals. The mixture of nitric and sulphuric acids (p. 303) converts them into esters of nitric acid—the nitro-compounds (p. 473). The acetyl esters are best obtained by heating them with acetic anhydride and sodium acetate (or $ZnCl_2$). Five acetyl groups are thus introduced (B. **22**, 2207). The benzoyl esters are prepared with even less difficulty, it being only necessary to shake the hexoses with benzoyl chloride and caustic soda (p. 304). Pentabenzoyl derivatives are then formed (B. **22**, R. 668; **24**, R. 971).

An elementary analysis will not yield a positive conclusion as to the number of acidyls that have entered compounds like those just mentioned. This is ascertained by first saponifying them with titrated alkali solutions, or, better, with magnesia (B. **12**, 1531). Or, the acetic esters are decomposed by boiling them with dilute sulphuric acid. The acetic acid that distils over is then titrated (A. **220**, 217; B. **23**, 1442). The presence of hydroxyl in the glucoses may also be proved by means of phenylisocyanate, with which they form carbanilic esters (B. **18**, 2606).

(5) Alkyl-sulphuric acids result upon treating the glucoses with chlorosulphonic acid, $ClHSO_3$. This is similar to the behavior of alcohols when exposed to like treatment (B. **17**, 2457).

The following reactions show the *aldehyde* and *ketone character* of the hexoses:

(1) By *reduction* (action of sodium amalgam) they become hexahydric alcohols. d-Mannose and d-fructose yield d-mannitol, galactose yields dulcitol, and d-sorbite seems to result from the reduction of d-glucose (grape-sugar).

(2) The *oxidation* of the hexoses does not occur directly upon exposure to the air. Oxidizing agents are necessary. Hence they show feeble *reducing* power. They precipitate the noble metals from solutions of their salts, and even reduce ammoniacal silver solutions in the cold. A very marked characteristic is their ability to precipitate cuprous oxide from warm alkaline cupric solutions (this is accelerated by tartaric acid). One molecule of hexose precipitates about five atoms of copper, as Cu_2O. This is the basis of the volumetric method for the estimation of the glucoses by means of Fehling's solution. Maltose and milk-sugar, of the di- and polysaccharides, only act directly upon the application of heat. The others must be first converted into glucoses (p. 573).

To prepare Fehling's solution, dissolve 34.65 grams of crystallized copper sulphate in water, then add 200 grams Rochelle salt and 600 c.cm. of NaOH (sp. gr. 1.1200), and dilute the solution to 1 litre. 0.05 gram hexose is required to completely reduce 10 c.c. of this liquid. The end reaction is rather difficult to recognize, hence it is frequently recommended to estimate the separated cuprous oxide gravimetrically (B. **13**, 826; **27**, R. 607, 760; **29**, R. 802). Consult B. **23**, 1035, for Soldaini's suggestion of using a copper carbonate solution for the estimation of the hexoses.

The hexoses are converted into their corresponding monocarboxylic acids (p. 564) by moderated oxidation with chlorine and bromine water, or silver oxide. More energetic oxidation changes them (as well as nearly all carbohydrates) to saccharic or mucic acids. Milk-sugar yields both acids at the same time.

The aldohexoses produce a red coloration in a sulphite-fuchsine solution, while the aldoketoses, like fructose and sorbinose, do not show this reaction (B. **27**, R. 674). The penta-acetyl and pentabenzoyl derivatives of the dextroses and galactoses no longer show the aldehyde character (B. **21**, 2842; **22**, R. 669). Hence, it was supposed that the hexoses possessed a constitution like ethylene oxide or a lactone (B. **22**, 2211; **21**, 2841; **23**, 2114; **26**, 2403; **28**, 3080).

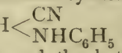
(3) The aldoses yield mercaptals with mercaptans, in the presence of hydrochloric acid (B. **27**, 673).

(4) Oximes are produced when alcoholic hydroxylamine acts upon the hexoses. To break down the aldoses the acetyl oxyacid nitriles,

obtained from the aldoximes and acetic anhydride, are split into prussic acid and acetyl pentoses (p. 535) (B. **24**, 993; **26**, 730).

(5*a*) Osamines are formed when the hexoses are acted upon with methyl alcoholic ammonia.

(5*b*) The hexoses and aniline, as well as its homologues, yield the anilides—*e. g.*, dextrose anilide, $CH_2OH[CH.OH]_4CH : N.C_6H_5$, which form cyanides with CNH—*e. g.*, anilidodextrose-cyanide, $CH_2OH[CH.OH]_4.CH<^{CN}_{NHC_6H_5}$ (B. **27**, 1287).



(6) Hydrazine converts the aldohexoses into aldazines, and the ketohexoses into ketazines (p. 220) (B. **29**, 2308).

(7) The phenylhydrazine derivatives are especially interesting (pp. 192, 207, 328). If one molecule of the phenylhydrazine (acetate) is allowed to act, the first product will be a *hydrazone*, $C_6H_{12}O_5.(N.-NH.C_6H_5)$. This class of compounds dissolves readily in water (with the exception of those derived from the mannoses and the higher glucoses, B. **23**, 2118). They generally crystallize from hot alcohol in colorless needles. Cold concentrated hydrochloric acid resolves them into their components. Benzaldehyde is also an excellent reagent for the decomposition of the phenylhydrazones (A. **288**, 140).

Diphenylhydrazine, $H_2N.N(C_6H_5)_2$, often produces diphenylhydrazones, $C_6H_{12}O_5 : N_2(C_6H_5)_2$ (B. **23**, 2619).

In the presence of an excess of phenylhydrazine the hexoses, like all glucoses, combine with two molecules of it upon application of heat and form the **osazones** (E. Fischer):

$$C_6H_{12}O_6 + 2H_2N.NH.C_6H_5 = \underset{\text{Glucosazone.}}{C_6H_{10}O_4(N.NH.C_6H_5)_2} + 2H_2O + H_2.$$

The reaction is carried out by adding two parts of phenylhydrazine, two parts of 50% acetic acid, and about twenty parts of water to one part of glucose. This mixture is digested for about one hour upon the water bath. The osazone then separates in a crystalline form (B. **17**, 579; **20**, 821; **23**, 2117). In this reaction a hydrazone is first produced, and one of its alcohol groups, adjacent to either an aldehyde or ketone group, is oxidized to CO (inasmuch as two hydrogen atoms in the presence of phenylhydrazine produce aniline and ammonia), which then acts further upon a second molecule of phenylhydrazine. *One* and the *same* **glucosazone,** $CH_2(OH).(CH.OH)_3.C(N_2H.C_6H_5).CH(N_2H.C_6H_5)$ (see B. **23**, 2118), is thus obtained from d-mannose, d-glucose, and d-fructose. This would indicate that the four carbon atoms which did not enter into reaction with phenylhydrazine contain the atoms or groups of atoms with which they are combined similarly arranged.

The osazones are yellow-colored compounds (see tartrazine, p. 528). They are usually insoluble in water, dissolve with difficulty in alcohol, and crystallize quite readily. When glucosazone is reduced with zinc dust and acetic acid it becomes isoglucosamine (p. 552). Nitrous acid converts the latter into fructose (B. **23**, 2110). The reformation of the hexoses from their osazones is readily effected by digestion with concentrated hydrochloric acid; they are then resolved into phenylhydrazine and the **osones** (B. **22**, 88; **23**, 2120):

$$\underset{\text{Glucosazone}}{C_6H_{10}O_4(N_2H.C_6H_5)_2} + 2H_2O =$$

$$\underset{\text{Glucosone.}}{CH_2(OH).(CH.OH)_3.CO.COH} + 2N_2H_3.C_6H_5.$$

The osones dissolve readily in water, and have not been obtained free. They combine, like ketone-aldehydes, with two molecules of phenylhydrazine and form osazones. They are converted into glucoses by reduction (when digested with zinc dust and acetic acid). In this way fruit-sugar is prepared from glucosazone (B. **23**, 2121).

The osones, like all ortho-dicarbonyl compounds, yield quinoxalines (B. **23**, 2121) with the orthodiamines. The glucoses also combine directly with the ortho-phenylenediamines (B. **20**, 281).

(8) Benzoyl hydrazide, or benzhydrazide, $NH_2 . NH . CO . C_6H_5$, combines with the aldohexoses to benzosazones, which contain four benzhydrazide residues (B. **29**, 2310):

$$C_6H_{12}O_6 + 4NH_2 . NH . CO . C_6H_5 = C_6H_6O_2(H . NH . COC_6H_5)_4 + 4H_2O + 3H_2.$$

(9) Being aldehydes or ketones, the hexoses combine with hydrocyanic acid, forming cyanhydrins, which yield monocarboxylic acids (p. 567). Their lactones can in turn be reduced to aldoses, whereby the synthesis of the monoses is achieved. Usually in the hydrogen cyanide addition the nitriles of both the acids possible theoretically are produced, but not in equal amounts.

These two reactions: (1) the hydrogen cyanide addition to the aldoses, and (2) reduction of the lactones of the oxycarboxylic acids, obtained from the nitriles, by means of sodium amalgam make possible the genetic connection of the following aldoses (B. **27**, 3192):

$$\begin{tikzcd}
 & \text{l-Mannose} \arrow[r] & \text{l-Mannoheptose} & \\
\text{l-Arabinose} \arrow[ur] \arrow[dr] & & & \\
 & \text{l-Glucose} & & \\
 & \text{l-Idose} & & \\
\text{l-Xylose} \arrow[ur] \arrow[dr] & & & \\
 & \text{l-Gulose} & & \\
\text{Rhamnose} \arrow[r] & \text{d-Rhamnohexose} \arrow[r] & \text{Rhamnoheptose} \arrow[r] & \text{Rhamno-octose} \\
\text{d-Mannose} \arrow[r] & \text{d-Mannoheptose} \arrow[r] & \text{d-Manno-octose} \arrow[r] & \text{d-Mannononose} \\
 & & \alpha\text{-Gluco-octose} \arrow[r] & \text{Gluconononose} \\
 & \alpha\text{-Glucoheptose} \arrow[ur] \arrow[dr] & & \\
\text{d-Glucose} \arrow[ur] \arrow[dr] & & \beta\text{-Gluco-octose} & \\
 & \beta\text{-Glucoheptose} & & \\
 & \alpha\text{-Galaheptose} \arrow[r] & \text{Galaoctose} & \\
\text{d-Galactose} \arrow[ur] \arrow[dr] & & & \\
 & \beta\text{-Galaheptose} & &
\end{tikzcd}$$

(10) *Fermentation of the Hexoses.*—The ready fermentation of the hexoses when exposed to the action of *schizomycetes* is characteristic of them. They sustain various decompositions.

1. The *alcoholic fermentation* of the hexoses is the most important decomposition of some of the aldohexoses. It is induced by yeast cells. d-Glucose or grape-sugar, d-mannose, d-galactose, and the keto-hexoses, d-fructose or fruit-sugar, are affected in this manner. This subject was exhaustively considered under ethyl alcohol (p. 120). The other hexoses are not altered by the yeast fungi (B. **27**, 2030).

2. In the *lactic acid* fermentation, the hexoses, milk-sugar, and gums decompose directly into lactic acid:

$$C_6H_{12}O_6 = 2C_3H_6O_3.$$

The active agents are little, wand-like organisms (bacteria and micrococci). Decaying albuminous matter (decaying cheese) is requisite for their development, and it only proceeds in liquids which are not too acid (p. 335). The temperature most favorable varies from 30–50°. By prolonged fermentation the lactates suffer *butyric fermentation;* this is owing to the appearance of other bacilli (p. 247): $2C_3H_6O_3 = C_4H_8O_2 + 2CO_2 + 2H_2$.

3. In *mucous fermentation* chain-like cells (of 0.001 mm. diameter) appear. These convert grape-sugar, with evolution of carbon dioxide, into a mucous, gummy substance; mannitol and lactic acid are formed at the same time.

2 A. ALDOHEXOSES.

(1) **Mannose,** $C_6H_{12}O_6$, is the aldehyde of mannitol. Like the latter, it exists in three forms (p. 540): dextro-, lævo-, and inactive [d + l] mannose (spacial formulas, p. 558; constitution, p. 561).

d-*Mannose*, *Seminose*, melting at 136°, was first prepared by oxidizing ordinary d-mannitol (together with d-fructose) with platinum black or nitric acid (B. **22**, 365). It is also obtained from salep mucus, and most easily from seminine (reserve-cellulose), occurring in different plant seeds, when this is boiled with dilute sulphuric acid (hence called *seminose*) (B. **22**, 609, 3218). d-Mannonic acid yields it upon reduction. It reduces Fehling's solution, and is fermented by yeast (B. **22**, 3223). When treated with alkalies it changes partly to d-glucose and d-fructose (B. **28**, 3078). Its *hydrazone* dissolves with difficulty in water, and melts at 195°. Benzaldehyde decomposes it into pure crystallized d-mannose (B. **29**, R. 913). Its *osazone*, $C_6H_{10}O_4(N_2H . C_6H_5)_2$, is identical with d-glucosazone. d-*Mannosoxime* melts at 184° (B. **24**, 699). Nascent hydrogen converts it into d-mannitol. Bromine oxidizes it to d-mannonic acid. Hydrocyanic acid causes it to pass into d-mannoheptonic acid (p. 567).

Methyl-d-Mannoside, $C_6H_{11}O_6 . CH_3$, melts at 190°, $[a]^{20°}_{d} = + 79.2°$ (B. **29**, 2928).

d-*Mannose-ethylene Mercaptal*, $C_6H_{12}O_5 : S_2C_2H_4$, melts at 153° (B. **29**, 549).

l-Mannose results when l-mannonic acid (its lactone) is reduced (p. 566, B. **23**, 373). It is very similar to the preceding compound, but is lævo-rotatory, and is fermented with more difficulty. Its *hydrazone* also dissolves with difficulty, and melts at 195°. It unites with two molecules of phenylhydrazine to form l-glucosazone (see below). It becomes l-mannitol by reduction. **Methyl-l-mannoside** melts at 190°; $[a]^{20°}_{d} = -79.4°$ (B. **29**, 2929).

[d + l] **Mannose** is formed (1) by the oxidation of *a*-acrite or [d + l] mannitol (p. 541), which can be obtained by the reduction of synthetic *a*-acrose or [d + l] fructose; (2) by the reduction of inactive [d + l] mannonic acid. It is quite similar to the two preceding compounds, but is inactive. Its *hydrazone* dissolves with difficulty, melts at 195°, and is inactive. Its osazone is i-glucosazone, identical with *a*-acrosazone. Yeast decomposes it, the d-mannose is fermented, and l-mannose remains (B. **23**, 382). *Methyl* [d + l] *mannoside*, melting at 165°, is obtained from the solution of equal quantities of its components at 15°. Below 8° the components crystallize out separately (B. **29**, 2929).

(2) **Glucose,** $C_6H_{12}O_6$, is probably the aldehyde of sorbite, and occurs as dextro-, lævo-, and inactive [d + l] glucose (p. 558).

d-**Glucose,** or *Grape Sugar*, formerly called *dextrose*, occurs (always with fruit sugar) in many sweet fruits and in honey; also in the urine in *Diabetes mellitus*. It is formed by the hydrolytic decomposition of poly-saccharides (cane sugar, starch, cellulose) and glucosides. It is prepared on a large scale by boiling starch with dilute sulphuric acid (see B. **13**, 1761). *The synthesis of grape sugar has been made possible by the production of glucose in the reduction of the lactone of d-gluconic acid* (p. 566).

Commercial grape sugar is an amorphous, compact mass, containing only about 60 per cent. glucose, along with a dextrine-like substance (gallesine, $C_{12}H_{24}O_{10}$), which is not fermentable (B. **17**, 2456).

The best method for preparing pure crystallized grape sugar consists in adding to 80 per cent. alcohol, mixed with $\frac{1}{15}$ volume fuming hydrochloric acid, finely pulverized cane sugar, as long as the latter dissolves on shaking (J. pr. Ch., **20**, 244).

Grape sugar crystallizes from water at the ordinary temperature, or dilute alcohol, with one molecule of water, in nodular masses, melting at 86°; at 110° it loses its water of crystallization. At 30–35° it crystallizes from its concentrated aqueous solution, and from its solution in ethyl or methyl alcohol, in anhydrous, hard crusts, melting at 146° (B. **15**, 1105).

Grape sugar is not quite so sweet to the taste as cane sugar, and serves to doctor wines.

Aqueous grape sugar is dextro-rotatory $[\alpha]_D = 52.6°$, and exhibits *bi-rotatory* power, *i. e.*, the freshly prepared solution deviates the polarized ray almost twice as strongly as it does after standing some time. At ordinary temperatures the deviation does not become constant until the expiration of twenty-four hours, whereas when boiled it does so in the course of a few minutes. The change in rotation is due to the production of different oxide-modifications (B. **28**, R. 461), when probably a non-asymmetric carbon atom becomes asymmetric (B. **28**, 3081; **29**, 203). Furthermore, the specific rotation of dextrose is appreciably augmented by concentration (B. **17**, 2234). This is dependent upon the decomposition of more complex crystal-molecules into normal molecules. This has been proved by determining the molecular weight by the method of Raoult (B. **21**, R. 505).

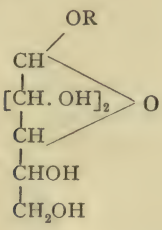
Grape sugar exhibits all the properties of the aldoses (p. 544). *α*- and *β-Phenylhydrazone* melt at 145° and at 116° (B. **22**, R. 669).

d-*Glucosazone* melts at 145°; the *β*-variety at 204–205°. Its aqueous solution is lævo-rotatory. *It may also be prepared from d-mannose and d-fructose*, as well as from glucosamine and isoglucosamine. Concentrated hydrochloric acid converts d-glucosazone into phenylhydrazine and *glucosone*, $C_6H_{10}O_6$ (p. 546); which regenerates d-glucosazone with two molecules of phenylhydrazine. It is a non-fermentable syrup, and if it be reduced with zinc and acetic anhydride, is converted into fruit sugar (= d-fructose) (B. **22**, 88).

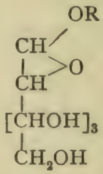
When grape sugar is reduced it yields d-sorbite, and when oxidized, d-gluconic acid and d saccharic acid. An alkaline copper solution converts it into formic acid, oxalic acid, tartronic acid, lactic acid, glyceric acid, and pyrocatechin (B. **27**, R. 788). Hydrocyanic acid changes it to glucose carboxylic acids (p. 568), and lime water to saccharonic acid. It is partially changed to d-mannose and d-fructose by alkalies (B. **28**, 3078).

Saccharates.—With baryta and lime grape sugar forms saccharates, like $C_6H_{12}O_6 \cdot CaO$, and $C_6H_{12}O_6 \cdot BaO$. These are precipitated by alcohol. With NaCl it forms large crystals, $2C_6H_{12}O_6 \cdot NaCl + H_2O$, which sometimes separate in the evaporation of diabetic urine.

Alkyl-d-glucosides.—The glucosides are the ethereal derivatives of the glucoses. Those of grape sugar particularly are frequently found in the vegetable kingdom. They generally contain the residues of aromatic bodies, and therefore will be discussed later. The simplest glucosides are the alkyl ethers of the sugars, which are produced in the action of HCl upon alcoholic sugar solutions (B. **28**, 1151). Fehling's solution and phenylhydrazine at 100° do not affect the alkyl-d-glucosides. However, they are decomposed into their components when boiled with dilute acids. These properties argue for the alkylen-oxide formulas for the alkyl glucosides (B. **28**, 3081), *e. g.:*



or



a- and *β*-**Methyl Glucoside,** $C_6H_{11}O_6 . CH_3$, melting at 165° and 107°, differ stereochemically. They are simultaneously formed in the action of hydrochloric acid and methyl alcohol upon grape sugar. The *a*-body is decomposed by invertin, but this is not the case with the *β*-compound (B. **27**, R. 885; **27**, 2479, 2985; **28**, 1145).

d-**Glucose Mercaptal,** $C_6H_{12}O_5(SC_2H_5)_2$, melting at 127°, is obtained from d-glucose, mercaptan, and HCl. d-**Glucose-ethylene Mercaptal,** $C_6H_{12}O_5 : S_2C_2H_4$, melts at 143°. d-**Glucose-trimethylene Mercaptal,** $C_6H_{12}O_5 : S_2C_3H_6$, melts at 130°. d-**Glucosebenzyl Mercaptal,** $C_6H_{12}O_5(SCH_2 . C_6H_5)_2$, melts at 133° (B. **29**, 547).

d-**Glucose Monacetone,** $C_6H_{10}O_6 : C(CH_3)_2$, melts at 156°.

d-**Glucose Diacetone,** $C_6H_8O_6[C(CH_3)_2]_2$, melts at 107° (B. **28**, 2496).

d-**Chloralose,** melting at 189°, and d-**Parachloralose,** $C_8H_{12}Cl_3O_6$, melting at 227°, are two isomeric bodies, produced by the rearrangement of d-glucose with chloral (B. **27**, R. 471; **29**, R. 177).

d-**Acetochlorhydrose,** $C_6H_7O(OCOCH_3)_4Cl$, results on heating d-glucose with acetyl chloride, and has been employed in the synthesis of d-glucosides.

d-**Glucosoxime,** $C_6H_{12}O_5NOH$, melting at 137°, when acted upon with acetic anhydride and sodium acetate, yields pentacetyl-d-glucono-nitrile (p. 566), from which d-arabinose was isolated (p. 536). These are reactions which render possible the breaking-down of the aldoses.

d-*Glucose-amido-guanidine Chloride*, $C_6H_{12}O_5 . CN_4H_4 . HCl$, melting at 165°, is obtained from d-glucose and amido-guanidine chlorhydrate (B. **27**, 971).

d-*Glucose-aldazine*, $CH_2OH[CH . OH]_4CH : N—N : CH[CH . OH]_4CH_2OH$, is very hygroscopic (B. **29**, 2308).

l-**Glucose** is formed when the lactone of l-gluconic acid is reduced. It is perfectly similar to grape sugar. It melts at 143°, but is lævo-rotatory, $[a]_D = —51.4°$. Its glucosazone is, however, dextro-rotatory. Its *diphenylhydrazone*, $C_6H_{12}O_5 : N . N(C_6H_5)_2$, dissolves with difficulty, and melts at 163° (B. **23**, 2618).

[d + l]-**Glucose** results from the union of d- and l-glucose, and by the reduction of [d + l]-gluconic lactone. Phenylhydrazine converts it into [d + l]-*glucosazone*, $C_6H_{10}O_5(N_2H . C_6H_5)_2$. This may also be obtained from i-mannose. It crystallizes in yellow needles, melting at 217–218°. The same [d + l]-glucosazone is produced from synthetic *a*-acrose ([d + l]-fructose), d-mannose, d-glucose, and d-fructose (fruit-sugar) (B. **23**, 383, 2620).

Glucosamine, $C_6H_{13}NO_5$, is produced on warming chitine (found in lobster shells), germ cellulose of *Boletus edulis*, with concentrated HCl (B. **17**, 243). Nitric acid oxidizes it to isosaccharic acid (p. 571) (B. **19**, 1257; **20**, 2569), and nitrous acid to chitose (B. **27**, 140). It forms d-glucosazone with phenylhydrazine.

Glucosamine-Oxime Hydrochloride, $C_6H_{11}O_4(NH_2)(NOH)HCl$, melts at 166° (B. **29**, 1392).

(3) **Gulose**, $CH_2OH[CHOH]_4CHO$ (space formula, pp. 558, 559), the second aldehyde of sorbite, is likewise known in its three modifications. They are formed by the reduction of the lactones of the three gulonic acids (p. 566), and by further reduction yield the sorbites. They are syrups and are not fermented by yeast. The name gulose is intended to indicate their relationship to glucose, the first aldehyde of sorbite. l- and [d + l] *Gulose Phenylhydrazone* melts at 143°. l-*Gulosazone* melts at 156°. [d + l] *Gulosazone* melts at 157–159°.

(4) d- and l-**Idoses** are prepared by the reduction of the idonic acids or their lactones (p. 567). They yield d- and l-idite on reduction (p. 541) (space formula, p. 558).

(5) **Galactose**, the aldehyde of inactive dulcite (p. 541), formed by intramolecular compensation, is known in three varieties. The [d + l] *galactose*, melting at 140–142°, results from the reduction of the lactone of [d + l] galactonic acid, and when fermented with beer yeast it becomes l-galactose. Its *phenylhydrazone* melts at 158–160°; its *osazone* at 206°.

l-*Galactose*, melting at 162–163° (see p. 559), yields dulcite in reduction, and mucic acid when it is oxidized. Its phenylhydrazone melts at 158–160°; its osazone melts at 206°.

d-*Galactose*, $CH_2OH[CHOH]_4CHO$, melting at 160°, is dextro-rotatory and fermentable (B. **21**, 1573) (see also p. 559; B. **27**, 383). It is formed along with d-glucose in the hydrolysis of milk sugar, of *galactite*, $C_9H_{18}O_7$, a beautifully crystallized body (B. **29**, 896), and of various gums (called galactans) (B. **20**, 1003), which nitric acid oxidizes to mucic acid. In preparing it, boil milk sugar with dilute sulphuric acid (A. **227**, 224). Dulcite is formed by its reduction, and galactonic and mucic acids by its oxidation. CNH and hydrochloric acid change it to galactose carboxylic acid (p. 568). α- and β-**Methyl-d-galactoside** melt at 111° and 173–175°. Emulsion decomposes the second (B. **28**, 1429). **Galactochloral** melts at 202° (B. **29**, R. 544). **Galactosamine** (B. **29**, R. 594). The *oxime* melts at 175°. The *osazone* melts at 193°. **Galactose amidoguanidine chloride** (B. **28**, 2613). The *pentacetyl* derivative melts at 142° (B. **22**, 2207). The *ethyl mercaptal* melts at 127°. The *ethylene mercaptal* melts at 149° (B. **29**, 547).

(6) d-**Talose**, $CH_2OH[CHOH]_4CHO$, is formed by the reduction of the lactone of d-talonic acid (p. 567) (B. **24**, 3625). Space formula, p. 559; compare B. **27**, 383.

(7) **Rhamnohexose**, *Methyl Hexose*, $CH_3 . CHOH[CHOH]_4 . CHO$, melting at 181°, is produced by the reduction of rhamnose carboxylic acid. The *osazone* melts at 200°. It forms methyl heptonic acid with hydrocyanic and hydrochloric acids.

3 A. KETOHEXOSES.

1. **Fructose**, $CH_2OH[CHOH]_3CO . CH_2OH$, occurs as d-, l-, and [d + l] varieties.

d-**Fructose, Fruit Sugar, Lævulose** (space formula, p. 563), melting at 95°, crystallizes with difficulty, and occurs in almost all sweet fruits, together with grape sugar. It was discovered in 1847 by Dubrimfaut. It is formed, (1) together with an equal amount of grape sugar, in the decomposition of cane sugar, and is separated from the latter through the insolubility of its calcium compound (B. **28**, R. 46). As fruit sugar rotates the plane of polarization more strongly toward the left than grape sugar does to the right, in the decomposition of the d-cane sugar a lævorotatory *invert sugar* solution (p. 120) results.

(2) Exclusively from inuline, on heating it with water to 100° for twenty-four hours, when it is completely changed to lævulose (A. **205**, 162; B. **23**, 2107). It can also be obtained from secalose, a carbohydrate contained in green barley plants (B. **27**, 3525).

(3) It is formed together with d-mannose in the oxidation of d-mannitol.

(4) From d-glucosazone, which has been prepared from d-glucose or grape sugar, as well as from d-mannose. *This method of formation allies fruit sugar genetically with d-glucose and d-mannose* (p. 548). Hence, in spite of its lævorotation of $[\alpha]_D = -71.4°$ (B. **19**, 393), it is called d-fructose. Fruit sugar dissolves with greater difficulty than grape sugar. By reduction it yields d-mannitol and d-sorbite, and when oxidized the products are trioxybutyric acid and glycollic acid. It is partially converted into d-glucose and d-mannose by alkalies (B. **28**, 3078). Heated under pressure with a little oxalic acid, d-fructose becomes β-oxy-δ-methyl furfurol (B. **28**, R. 786). It yields d-fructose carboxylic acid (p. 568) when treated with hydrocyanic and hydrochloric acids; this may be reduced to methyl butylacetic acid, and thus the constitution of fruit sugar is proved. Phenylhydrazine and fructose yield d-glucosazone, which changes by reduction to *isoglucosamine* or d-*fructosamine*, $CH_2OH[CH . OH]_3CO . CH_2 . NH_2$ (B. **20**, 2571).

Methyl-d-fructoside (B. **28**, 1160), *lævulo-chloral*, melts at 228° (B. **29**, R. 544).

l-**Fructose** is produced by fermenting [d + l] fructose (α-acrose) with yeast (B. **23**, 389).

[d + l] **Fructose** or α-**Acrose**.—Sodium amalgam converts it into *α-acrite*, identical with i-mannitol. Yeast breaks it up, leaving l-fructose. Its *osazone* is identical with i-glucosazone, from which i-fructose can again be regenerated. α-Acrite can also yield i-mannonic acid, and the latter fruit sugar and grape sugar.

The fructose modification, which can be resolved, is, by virtue of its synthetic formation, of the greatest importance in the synthesis of sugars (p. 553).

Historical.—**Methylenitan** was the first compound, resembling the sugars, that was prepared. Butlerow (1861) obtained it by condensing trioxymethylene (p. 194) with lime water. O. Loew (1885) obtained *formose* (J. pr. Ch. **33**, 321) in an analogous manner from oxymethylene, and somewhat later the fermentable *methose*, by the use of magnesia (B. **22**, 470, 478). E. Fischer considers these three compounds mixtures of different glucoses, among which α-acrose occurs (B. **22**, 360). The latter (together with β-acrose) is obtained by the action of barium hydroxide upon acroleïn bromide, $C_3H_5OBr_2$ (E. Fischer and J. Tafel), and by the condensation of so-called glycerose (p. 477), a mixture of $CH_2OH . CHOH . CHO$ and $CH_2OH . CO . CH_2OH$, obtained by the careful oxidation of glycerol (B. **23**, 389, 2131). By reduction with sodium amalgam α-acrose (identical with [d + l] fructose) passes into α-acrite, identical with [d + l] mannitol.

2. **Sorbinose**, *Sorbose*, $C_6H_{12}O_6$, is found in mountain-ash berries. It is incapable of fermentation under the influence of yeast. Oxidized with nitric acid it yields trioxyglutaric acid. Its osazone, *sorbinosazone*, melts at 164°. **Methyl Sorboside** melts at 120–122° (B. **28**, 1160).

2B. ALDOHEPTOSES, 2C. ALDO-OCTOSES and 2D. ALDONONOSES
(E. Fischer, A. 270, 64).

Just as aldohexoses can be built up from aldopentoses, so can aldoheptoses be obtained from aldohexoses, and aldo-octoses from the aldoheptoses, etc.,—*e. g.*, hydrocyanic acid is added to d-mannose, the lactone of the d-mannoheptonic acid is then reduced to d-mannoheptose, which, subjected to the same reactions, yields d-manno-octose. The heptoses and octoses do not ferment. *Heptites*, *octites* and *nonites* are formed in their reduction (p. 542).

d-**Manno-heptose,** $C_7H_{14}O_7$, is obtained from the lactone of mannoheptonic acid (p. 567). Perseïte yields it when oxidized (p. 542). It melts at 135°. Its *hydrazone* dissolves with difficulty and melts about 198°. Its *osazone* melts near 200° (B. 23, 2231). Sodium amalgam converts it into perseïte (p. 542). l-**Manno-heptose** (A. 272, 186).

α-**Gluco-heptose,** $C_7H_{14}O_7$, melts about 190°. Its *osazone* melts about 195°. β-**Gluco-heptose** (A. 270, 72, 87).

α-**Gala-heptose,** $C_7H_{14}O_7$, from α-galaheptonic acid, forms an osazone melting about 220°. It yields gala-octonic acid (p. 567) with hydrocyanic and hydrochloric acids. β-**Gala-heptose** melts with decomposition about 190–194°, and is obtained from the lactone of β-galaheptonic acid (A. 288, 139).

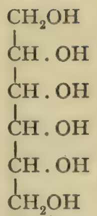
d-**Manno-octose,** $C_8H_{16}O_8$, is obtained from the lactone of manno-octonic acid (B. 23, 2234), and is syrup-like. α-**Gluco-octose** (A. 270, 95). α-**Galaoctose** (A. 288, 150).

d-**Manno-nonose,** $C_9H_{18}O_9$, the lactone of d-mannononic acid, is very similar to grape sugar. *It ferments under the influence of yeast.* The *hydrazone* melts at 223°, the *osazone* about 227° (B. 23, 2237). **Glucononose** (A. 270, 104).

THE SYNTHESIS OF GRAPE SUGAR OR d-GLUCOSE, AND OF FRUIT SUGAR OR d-FRUCTOSE.

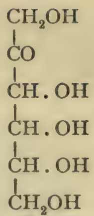
As repeatedly mentioned, E. Fischer succeeded in isolating α-**Acrose** or [d + l] **Fructose** from the condensation products of *glycerose* (p. 477) and *formaldehyde* (p. 193). In his hands this became the starting-out substance for the preparation not only of fruit sugar or d-fructose, and of grape sugar or d-glucose, but also of d-mannose, of ordinary or d-mannitol, and of ordinary or d-sorbitol, as well as of the l-modifications corresponding to the bodies just mentioned. The intimate connections between these substances are represented in a diagram given on p. 554.

Following the course laid down in this scheme, which finally culminated in the synthesis of fruit sugar and of grape sugar, the starting-out material is found to be *a-Acrose* or [d + l] *Fructose.* This is produced by the aldol condensation of glycerose, a mixture of the first oxidation products of glycerol, through the agency of caustic soda. The reduction of *a-acrose* yields *a-acrite* or [d + l] *mannitol*, which is arrived at in the following manner: When ordinary or d-*mannitol* is oxidized, d-*mannose* results, and the latter by similar treatment becomes d-*mannonic acid*, which readily passes into its *lactone*. l-Arabinose also, by rearrangement through prussic acid, becomes l-*arabinose-carboxylic acid* or l-*mannonic acid*. Its lactone combines with the lactone of d-mannonic acid and the product is the lactone of [d + l] mannonic acid. Upon reducing the three lactones in sulphuric acid solution with sodium amalgam, d-, l-, and [d + l] *mannose*, and d-, l-, and [d + l] *mannitol*, formed by the further reduction of the latter bodies, are produced. [d + l] *Mannitol is identical with a-acrite or a-acrose.* Therefore, [d + l] mannonic acid became a very suitable starting-out substance in realizing the second synthesis, because α-acrose is very hard to obtain in anything like a desirable quantity.



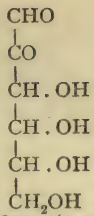
$$\begin{array}{l} CH_2OH \\ | \\ CH.OH \\ | \\ CH.OH \\ | \\ CH.OH \\ | \\ CH.OH \\ | \\ CH_2OH \end{array}$$

Hexite



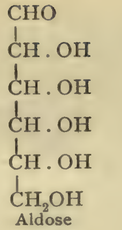
$$\begin{array}{l} CH_2OH \\ | \\ CO \\ | \\ CH.OH \\ | \\ CH.OH \\ | \\ CH.OH \\ | \\ CH_2OH \end{array}$$

Ketose



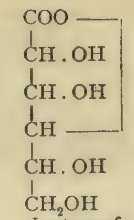
$$\begin{array}{l} CHO \\ | \\ CO \\ | \\ CH.OH \\ | \\ CH.OH \\ | \\ CH.OH \\ | \\ CH_2OH \end{array}$$

Osone (p. 546)

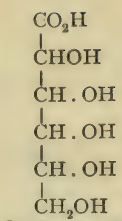


$$\begin{array}{l} CHO \\ | \\ CH.OH \\ | \\ CH.OH \\ | \\ CH.OH \\ | \\ CH.OH \\ | \\ CH_2OH \end{array}$$

Aldose

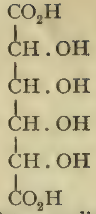


Lactone of Pentoxy-n-caproic Acid



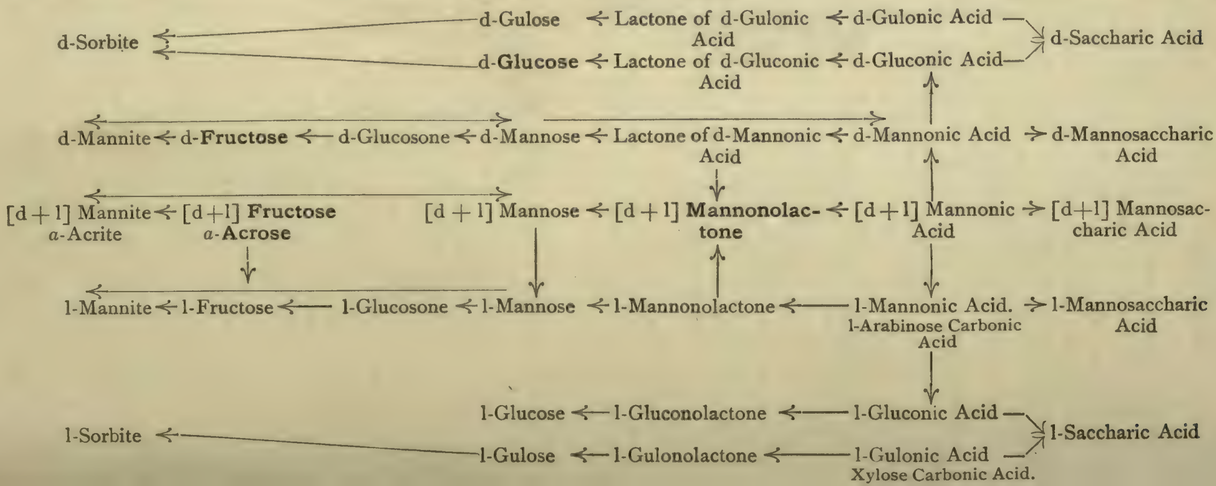
$$\begin{array}{l} CO_2H \\ | \\ CHOH \\ | \\ CH.OH \\ | \\ CH.OH \\ | \\ CH.OH \\ | \\ CH_2OH \end{array}$$

Pentoxy-n-caproic Acid



$$\begin{array}{l} CO_2H \\ | \\ CH.OH \\ | \\ CH.OH \\ | \\ CH.OH \\ | \\ CH.OH \\ | \\ CO_2H \end{array}$$

Tetraoxyadipic Acid.



The course from [d + l] mannonic acid divides in the same way to the d-derivatives as it does toward the l-compounds, because [d + l] mannonic acid, like racemic acid (p. 523), can be resolved by strychnine and morphine into d- and l-mannonic acid. By the reduction, on the one hand, of the lactone of d-mannonic acid, d-*mannose* and d-*mannitol* are formed, and on the other hand, d-mannose and phenylhydrazine yield d-glucosazone, which can also be obtained from grape sugar or d-glucose, and fruit sugar or d-fructose.

d-Glucosazone yields glucosone (p. 546), and the latter by reduction forms **fruit sugar or d-fructose.**

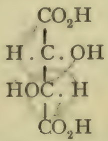
To pass from d-mannonic acid to d-glucose, heat the former to 140° with quinoline. It is then partially converted into d-*gluconic acid*. Conversely, the latter under the same conditions changes in part to d-mannonic acid. **d-Glucose or Grape Sugar** is formed in the reduction of the lactone of d-*gluconic acid*. d-Sorbite is produced when grape sugar is reduced. Proceeding from l-mannonic acid, the corresponding l-derivatives are similarly obtained. l-*Fructose* is also formed by the fermentation of [d + l] fructose or *a-acrose*, and l mannose in like manner from [d + l] mannose.

The gulose groups and the sugar-acids, produced in the oxidation of the pentaoxy-n caproic acids, are also considered in the table. d-Saccharic acid, resulting from the oxidation of d gluconic acid, becomes d-gulonic acid on reduction, and the lactone of the latter by similar treatment changes to d-*gulose*, the second aldehyde of d-sorbite.

The aldohexoses are connected with the aldopentoses (1) through l-*arabinose*, which, by the addition of CNH, as already mentioned, passes over into l-arabinose carboxylic acid or l-mannonic acid, and also into l-*gluconic acid;* (2) through the *xyloses*, the CNH-addition product of which is the nitrile of *xylose carboxylic acid*, or l-*gulonic acid*. Oxidation changes l-gulonic acid to l-saccharic acid. l-*Gulose* and l-*sorbite* are formed in the reduction of its lactone.

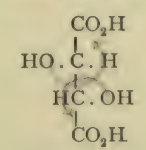
A. THE SPACE ISOMERISM OF THE PENTITES AND PENTOSES, THE HEXITES AND HEXOSES.

The structural formula of the normal, simplest pentite: $CH_2OH . \overset{*}{C}H . OH . CH.OH . \overset{*}{C}HOH . CH_2OH$, contains two asymmetric carbon atoms. The CHOH-group, standing between them is the cause of two possible inactive modifications instead of one (the case with the tartaric acids), as the result of an intramolecular compensation. Furthermore, theory permits of two optically active modifications, and a fifth optically inactive form, arising from the union of the two optically active varieties. This is the racemic or [d + l] modification, corresponding to [d + l] tartaric acid or racemic acid. These relations are most quickly and readily made clear by means of the atom models. The molecule-model is projected upon the surface of the paper, and then formulas similar to those observed with tartaric acid are derived:



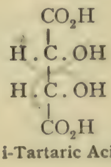
$$\begin{array}{c} CO_2H \\ | \\ H.C.OH \\ | \\ HOC.H \\ | \\ CO_2H \end{array}$$

d-Tartaric Acid



$$\begin{array}{c} CO_2H \\ | \\ HO.C.H \\ | \\ HC.OH \\ | \\ CO_2H \end{array}$$

l-Tartaric Acid



$$\begin{array}{c} CO_2H \\ | \\ H.C.OH \\ | \\ H.C.OH \\ | \\ CO_2H \end{array}$$

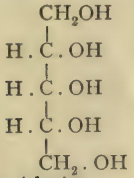
i-Tartaric Acid.

A. SPACE ISOMERISM OF THE PENTITES AND ALDOPENTOSES.

The formulas for the four stereochemically different pentites arise in the same manner as in the case of the tartaric acids. Suppose these four pentites to be oxidized, in one instance the upper CH_2OH group, and then the lower similar group having been converted into the CHO-group, there will result eight stereochemically different aldopentose formulas, none of which passes into any other by a rotation of 180°. The number of predicted space-isomerides with n-asymmetric carbon atoms, and with an asymmetric formula may be more easily deduced by applying the 2^n formula of van 't Hoff, in which n indicates the number of asymmetric carbon atoms. In the aldopentoses n = 3, hence $2^n = 2^3 = 8$:

Pentites (*and Trioxyglutaric Acids*).

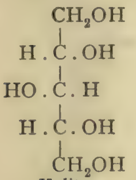
(1)



$$\begin{array}{c} CH_2OH \\ | \\ H.C.OH \\ | \\ H.C.OH \\ | \\ H.C.OH \\ | \\ CH_2.OH \end{array}$$

Adonite
(Ribotrioxyglutaric Acid)

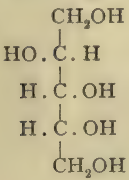
(2)



$$\begin{array}{c} CH_2OH \\ | \\ H.C.OH \\ | \\ HO.C.H \\ | \\ H.C.OH \\ | \\ CH_2OH \end{array}$$

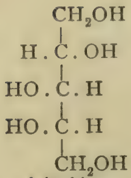
Xylite
(Xilotrioxyglutaric Acid)

(3)



$$\begin{array}{c} CH_2OH \\ | \\ HO.C.H \\ | \\ H.C.OH \\ | \\ H.C.OH \\ | \\ CH_2OH \end{array}$$

(4)

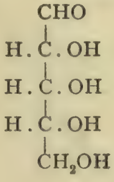


$$\begin{array}{c} CH_2OH \\ | \\ H.C.OH \\ | \\ HO.C.H \\ | \\ HO.C.H \\ | \\ CH_2OH \end{array}$$

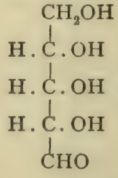
l-Arabite
(l-Trioxyglutaric Acid)

Aldopentoses (*and Penton-acids*).

(1^1)

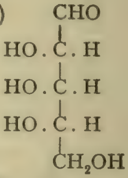


$$\begin{array}{c} CHO \\ | \\ H.C.OH \\ | \\ H.C.OH \\ | \\ H.C.OH \\ | \\ CH_2OH \end{array}$$



$$\begin{array}{c} CH_2OH \\ | \\ H.C.OH \\ | \\ H.C.OH \\ | \\ H.C.OH \\ | \\ CHO \end{array}$$

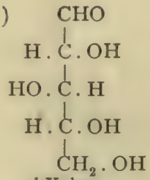
or (2^1)



$$\begin{array}{c} CHO \\ | \\ HO.C.H \\ | \\ HO.C.H \\ | \\ HO.C.H \\ | \\ CH_2OH \end{array}$$

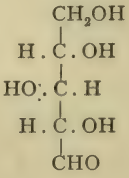
l-Ribose
(l-Ribonic Acid)

(3^1)



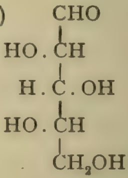
$$\begin{array}{c} CHO \\ | \\ H.C.OH \\ | \\ HO.C.H \\ | \\ H.C.OH \\ | \\ CH_2.OH \end{array}$$

l-Xylose
(l-Xylonic Acid)



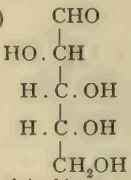
$$\begin{array}{c} CH_2OH \\ | \\ H.C.OH \\ | \\ HO.C.H \\ | \\ H.C.OH \\ | \\ CHO \end{array}$$

or (4^1)



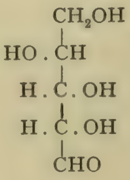
$$\begin{array}{c} CHO \\ | \\ HO.CH \\ | \\ H.C.OH \\ | \\ HO.CH \\ | \\ CH_2OH \end{array}$$

(5^1)



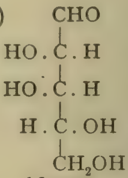
$$\begin{array}{c} CHO \\ | \\ HO.CH \\ | \\ H.C.OH \\ | \\ H.C.OH \\ | \\ CH_2OH \end{array}$$

d-Arabinose



$$\begin{array}{c} CH_2OH \\ | \\ HO.CH \\ | \\ H.C.OH \\ | \\ H.C.OH \\ | \\ CHO \end{array}$$

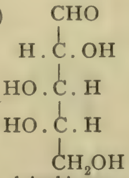
or (6^1)



$$\begin{array}{c} CHO \\ | \\ HO.C.H \\ | \\ HO.C.H \\ | \\ H.C.OH \\ | \\ CH_2OH \end{array}$$

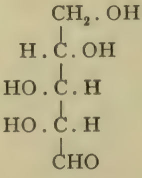
l-Lyxose

(7^1)



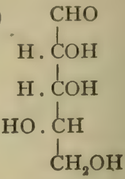
$$\begin{array}{c} CHO \\ | \\ H.C.OH \\ | \\ HO.C.H \\ | \\ HO.C.H \\ | \\ CH_2OH \end{array}$$

l-Arabinose
(l-Arabonic Acid)



$$\begin{array}{c} CH_2.OH \\ | \\ H.C.OH \\ | \\ HO.C.H \\ | \\ HO.C.H \\ | \\ CHO \end{array}$$

or (8^1)



$$\begin{array}{c} CHO \\ | \\ H.COH \\ | \\ H.COH \\ | \\ HO.CH \\ | \\ CH_2OH \end{array}$$

The image-isomeric aldopentoses are capable naturally of uniting to four inactive double molecules, which can be resolved. The space-formulas (7^1) and (3^1) for ordinary or l-arabinose and the xyloses follow from the intimate connection of the l-arabinoses with l-glucose, and the xyloses with l-gulose, as will be shown later (p. 562).

If the space formula of inactive xylite may be considered as established, there remains but one possible formula for inactive adonite, the reduction product of ribose.

Four *trioxyglutaric acids* (p. 538) correspond to the four theoretically predicted pentites. The same number of eight space isomerides as indicated by the pentoses are possible also for the corresponding monocarboxylic acids, the *tetra-oxy-n-valeric acids*, as well as for their corresponding aldehydo-carboxylic acids, and also for the *ketoses of the hexite series*, to which fruit sugar belongs.

B. THE SPACE ISOMERISM OF THE SIMPLEST HEXITES AND THE SUGARS, THE ALDOHEXOSES AND THE GLUCONIC ACIDS.*

The structural formula of the normal and simplest hexite:

$CH_2OH\ .\ \overset{*4}{C}H\ .\ OH\ .\ \overset{*3}{C}H\ .\ OH\ .\ \overset{*2}{C}H\ .\ OH\ .\ \overset{*1}{C}H\ .\ OH\ .\ CH_2OH$, contains four asymmetric carbon atoms. The theory of van't Hoff and Le Bel permits of ten possible space-isomeric configurations for such a compound.*

In tartaric acid we started with the point of union of the two asymmetric carbon atoms in determining the successive series; and in hexite also we begin in the middle of the molecule, and then compare C-atom 1 with C-atom 4, and C-atom 2 with C-atom 3. In this manner the ten hexite configurations given on p. 558 have been derived.

If we suppose each of the ten hexites to have been oxidized, in one instance the upper $—CH_2OH$ group, and again the lower $—CH_2OH$ group 2, to aldoses, then twenty space-isomeric aldohexoses would result. However, each of the four hexites (Nos. 1, 2, 3, and 4) yields two aldoses, whose formulas by a rotation of 180° pass into each other, which consequently would reduce the number of possible space-isomeric aldohexoses to 16.

Ten tetraoxyadipic acids (*saccharic acids*) correspond to the ten space-isomeric hexites; sixteen penta-oxy n-valeric acids or hexonic (*gluconic acids*), and sixteen aldehydo-tetraoxy-monocarboxylic acids (*glucuronic acids*) correspond to the sixteen space-isomeric aldohexoses.

The hexites and the tetraoxyadipic acids also have inactive, racemic or [d + l] modifications, the aldohexoses, hexonic acids, and aldehydotetraoxycarboxylic acids also 8 [d + l] modifications, as is evident from an inspection of the formulas in the appended table.

The number of theoretically possible space-isomeric aldohexoses, containing four asymmetric carbon atoms in the molecule, are more readily derived by employing the van 't Hoff formula 2^n given above with the aldopentoses. This for 2^4 would give sixteen space isomeric aldohexoses.

The space-isomerism of the ketohexoses, containing three asymmetric C-atoms, is like the isomerism of the aldopentoses.

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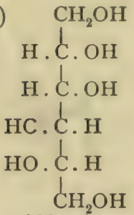
* Die Lagerung der Atome im Raum von J. H. van 't Hoff, and Grundriss der Stereochemie von Hantzsch (Breslau, 1893).

Hexites (*and Saccharic Acids*).

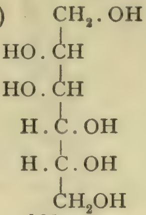
(1)



$$\begin{array}{rl} & \mathrm{CH_2OH} \\ \mathrm{H.} & \mathrm{C.OH} \\ \mathrm{H.} & \mathrm{C.OH} \\ \mathrm{HC.} & \mathrm{C.H} \\ \mathrm{HO.} & \mathrm{C.H} \\ & \mathrm{CH_2OH} \end{array}$$

l-Mannite
(l-Mannosaccharic Acid)

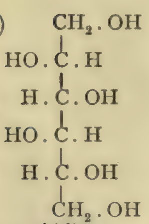
(2)



$$\begin{array}{rl} & \mathrm{CH_2.OH} \\ \mathrm{HO.} & \mathrm{CH} \\ \mathrm{HO.} & \mathrm{CH} \\ \mathrm{H.} & \mathrm{C.OH} \\ \mathrm{H.} & \mathrm{C.OH} \\ & \mathrm{CH_2OH} \end{array}$$

d-Mannite
(d-Mannosaccharic Acid)

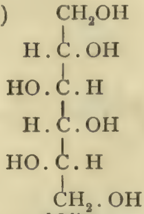
(3)



$$\begin{array}{rl} & \mathrm{CH_2.OH} \\ \mathrm{HO.} & \mathrm{C.H} \\ \mathrm{H.} & \mathrm{C.OH} \\ \mathrm{HO.} & \mathrm{C.H} \\ \mathrm{H.} & \mathrm{C.OH} \\ & \mathrm{CH_2.OH} \end{array}$$

l-Idite
(l-Idosaccharic Acid)

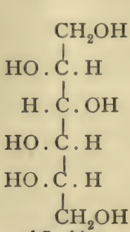
(4)



$$\begin{array}{rl} & \mathrm{CH_2OH} \\ \mathrm{H.} & \mathrm{C.OH} \\ \mathrm{HO.} & \mathrm{C.H} \\ \mathrm{H.} & \mathrm{C.OH} \\ \mathrm{HO.} & \mathrm{C.H} \\ & \mathrm{CH_2.OH} \end{array}$$

d-Idite
(d-Idosaccharic Acid)

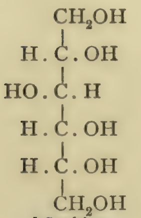
(5)



$$\begin{array}{rl} & \mathrm{CH_2OH} \\ \mathrm{HO.} & \mathrm{C.H} \\ \mathrm{H.} & \mathrm{C.OH} \\ \mathrm{HO.} & \mathrm{C.H} \\ \mathrm{HO.} & \mathrm{C.H} \\ & \mathrm{CH_2OH} \end{array}$$

l-Sorbite
(l-Saccharic Acid)

(6)

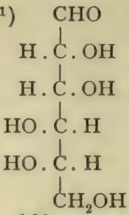


$$\begin{array}{rl} & \mathrm{CH_2OH} \\ \mathrm{H.} & \mathrm{C.OH} \\ \mathrm{HO.} & \mathrm{C.H} \\ \mathrm{H.} & \mathrm{C.OH} \\ \mathrm{H.} & \mathrm{C.OH} \\ & \mathrm{CH_2OH} \end{array}$$

d-Sorbite
(d-Saccharic Acid)

Aldohexoses (*and Hexonic Acids*).

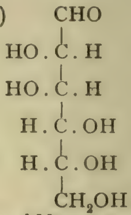
(1^1)



$$\begin{array}{rl} & \mathrm{CHO} \\ \mathrm{H.} & \mathrm{C.OH} \\ \mathrm{H.} & \mathrm{C.OH} \\ \mathrm{HO.} & \mathrm{C.H} \\ \mathrm{HO.} & \mathrm{C.H} \\ & \mathrm{CH_2OH} \end{array}$$

l-Mannose
(l-Mannonic Acid)

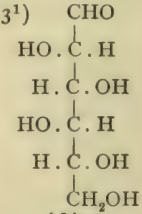
(2^1)



$$\begin{array}{rl} & \mathrm{CHO} \\ \mathrm{HO.} & \mathrm{C.H} \\ \mathrm{HO.} & \mathrm{C.H} \\ \mathrm{H.} & \mathrm{C.OH} \\ \mathrm{H.} & \mathrm{C.OH} \\ & \mathrm{CH_2OH} \end{array}$$

d-Mannose
(d-Mannonic Acid)

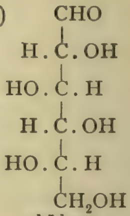
(3^1)



$$\begin{array}{rl} & \mathrm{CHO} \\ \mathrm{HO.} & \mathrm{C.H} \\ \mathrm{H.} & \mathrm{C.OH} \\ \mathrm{HO.} & \mathrm{C.H} \\ \mathrm{H.} & \mathrm{C.OH} \\ & \mathrm{CH_2OH} \end{array}$$

l-Idose
(l-Idonic Acid)

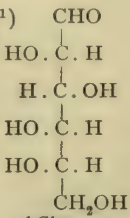
(4^1)



$$\begin{array}{rl} & \mathrm{CHO} \\ \mathrm{H.} & \mathrm{C.OH} \\ \mathrm{HO.} & \mathrm{C.H} \\ \mathrm{H.} & \mathrm{C.OH} \\ \mathrm{HO.} & \mathrm{C.H} \\ & \mathrm{CH_2OH} \end{array}$$

d-Idose
(d-Idonic Acid)

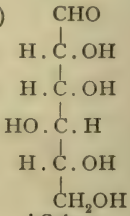
(5^1)



$$\begin{array}{rl} & \mathrm{CHO} \\ \mathrm{HO.} & \mathrm{C.H} \\ \mathrm{H.} & \mathrm{C.OH} \\ \mathrm{HO.} & \mathrm{C.H} \\ \mathrm{HO.} & \mathrm{C.H} \\ & \mathrm{CH_2OH} \end{array}$$

l-Glucose
(l-Gluconic Acid)

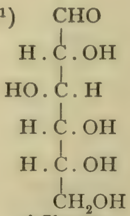
(6^1)



$$\begin{array}{rl} & \mathrm{CHO} \\ \mathrm{H.} & \mathrm{C.OH} \\ \mathrm{H.} & \mathrm{C.OH} \\ \mathrm{HO.} & \mathrm{C.H} \\ \mathrm{H.} & \mathrm{C.OH} \\ & \mathrm{CH_2OH} \end{array}$$

l-Gulose
(l-Gulonic Acid)

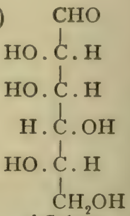
(7^1)



$$\begin{array}{rl} & \mathrm{CHO} \\ \mathrm{H.} & \mathrm{C.OH} \\ \mathrm{HO.} & \mathrm{C.H} \\ \mathrm{H.} & \mathrm{C.OH} \\ \mathrm{H.} & \mathrm{C.OH} \\ & \mathrm{CH_2OH} \end{array}$$

d-Glucose
(d-Gluconic Acid)

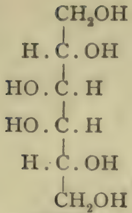
(8^1)



$$\begin{array}{rl} & \mathrm{CHO} \\ \mathrm{HO.} & \mathrm{C.H} \\ \mathrm{HO.} & \mathrm{C.H} \\ \mathrm{H.} & \mathrm{C.OH} \\ \mathrm{HO.} & \mathrm{C.H} \\ & \mathrm{CH_2OH} \end{array}$$

d-Gulose
(d-Gulonic Acid)

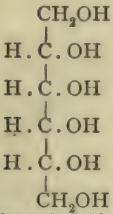
(7)



$$\begin{array}{c}\mathrm{CH_2OH}\\ |\\ \mathrm{H.C.OH}\\ |\\ \mathrm{HO.C.H}\\ |\\ \mathrm{HO.C.H}\\ |\\ \mathrm{H.C.OH}\\ |\\ \mathrm{CH_2OH}\end{array}$$

Dulcite
(Mucic Acid)

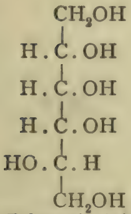
(8)



$$\begin{array}{c}\mathrm{CH_2OH}\\ |\\ \mathrm{H.C.OH}\\ |\\ \mathrm{H.C.OH}\\ |\\ \mathrm{H.C.OH}\\ |\\ \mathrm{H.C.OH}\\ |\\ \mathrm{CH_2OH}\end{array}$$

(Allomucic Acid ?)

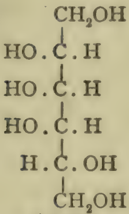
(9)



$$\begin{array}{c}\mathrm{CH_2OH}\\ |\\ \mathrm{H.C.OH}\\ |\\ \mathrm{H.C.OH}\\ |\\ \mathrm{H.C.OH}\\ |\\ \mathrm{HO.C.H}\\ |\\ \mathrm{CH_2OH}\end{array}$$

(l-Talomucic Acid)

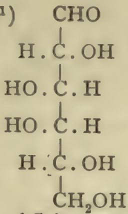
(10)



$$\begin{array}{c}\mathrm{CH_2OH}\\ |\\ \mathrm{HO.C.H}\\ |\\ \mathrm{HO.C.H}\\ |\\ \mathrm{HO.C.H}\\ |\\ \mathrm{H.C.OH}\\ |\\ \mathrm{CH_2OH}\end{array}$$

d-Talite
(d-Talomucic Acid)

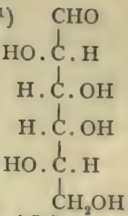
(9^1)



$$\begin{array}{c}\mathrm{CHO}\\ |\\ \mathrm{H.C.OH}\\ |\\ \mathrm{HO.C.H}\\ |\\ \mathrm{HO.C.H}\\ |\\ \mathrm{H.C.OH}\\ |\\ \mathrm{CH_2OH}\end{array}$$

d-Galactose
(d-Galactonic Acid)

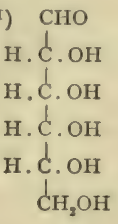
(10^1)



$$\begin{array}{c}\mathrm{CHO}\\ |\\ \mathrm{HO.C.H}\\ |\\ \mathrm{H.C.OH}\\ |\\ \mathrm{H.C.OH}\\ |\\ \mathrm{HO.C.H}\\ |\\ \mathrm{CH_2OH}\end{array}$$

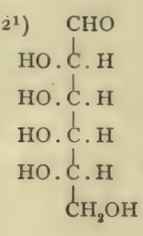
l-Galactose
(l-Galactonic Acid)

(11^1)



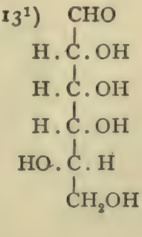
$$\begin{array}{c}\mathrm{CHO}\\ |\\ \mathrm{H.C.OH}\\ |\\ \mathrm{H.C.OH}\\ |\\ \mathrm{H.C.OH}\\ |\\ \mathrm{H.C.OH}\\ |\\ \mathrm{CH_2OH}\end{array}$$

(12^1)



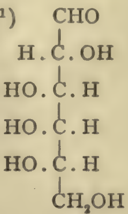
$$\begin{array}{c}\mathrm{CHO}\\ |\\ \mathrm{HO.C.H}\\ |\\ \mathrm{HO.C.H}\\ |\\ \mathrm{HO.C.H}\\ |\\ \mathrm{HO.C.H}\\ |\\ \mathrm{CH_2OH}\end{array}$$

(13^1)



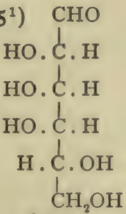
$$\begin{array}{c}\mathrm{CHO}\\ |\\ \mathrm{H.C.OH}\\ |\\ \mathrm{H.C.OH}\\ |\\ \mathrm{H.C.OH}\\ |\\ \mathrm{HO.C.H}\\ |\\ \mathrm{CH_2OH}\end{array}$$

(14^1)



$$\begin{array}{c}\mathrm{CHO}\\ |\\ \mathrm{H.C.OH}\\ |\\ \mathrm{HO.C.H}\\ |\\ \mathrm{HO.C.H}\\ |\\ \mathrm{HO.C.H}\\ |\\ \mathrm{CH_2OH}\end{array}$$

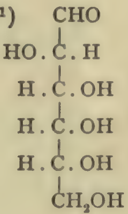
(15^1)



$$\begin{array}{c}\mathrm{CHO}\\ |\\ \mathrm{HO.C.H}\\ |\\ \mathrm{HO.C.H}\\ |\\ \mathrm{HO.C.H}\\ |\\ \mathrm{H.C.OH}\\ |\\ \mathrm{CH_2OH}\end{array}$$

d-Talose
(d-Talonic Acid)

(16^1)



$$\begin{array}{c}\mathrm{CHO}\\ |\\ \mathrm{HO.C.H}\\ |\\ \mathrm{H.C.OH}\\ |\\ \mathrm{H.C.OH}\\ |\\ \mathrm{H.C.OH}\\ |\\ \mathrm{CH_2OH}\end{array}$$

To render rational names possible, E. Fischer has proposed to indicate the configuration by the sign + or —. These are not intended to show the influence of the individual asymmetric carbon atom upon the optical properties of the molecule, as van 't Hoff formerly expressed it, but merely the position of a substituent upon the right or left side of the preceding configuration formulas. The formula should be so viewed that in the sugars the aldehyde or ketone group, and in the monobasic acids the carboxyls stand above. The numbers begin above, and the sign + or — represents the position of hydroxyl, *e. g.*:

Grape Sugar, d-Glucose = Hexanpentolal + — + + (Formula 7^1).
d-Gluconic Acid, . . . = Hexanpentol acid + — + + (Formula 7^1).
Fruit Sugar, d-Fructose = Hexanpentol-2-on — + +.

In the case of symmetrical structure,—as it exists, for example, in the diacids and alcohols of the sugar group,—there is no favored position; consequently, presuming that the numbering invariably proceeds from the top down, we get a doubled steric designation, *e. g.*:

d-Saccharic Acid, . . = Hexantetrol diacid + — + + or — — + —
Dulcite, ... = Hexanhexol, . . + — — + or — + + —

Derivation of the Space-formula for d-Glucose or Grape Sugar, the most important aldohexose. The following relations arranged first in the diagram are the basis of this derivation:

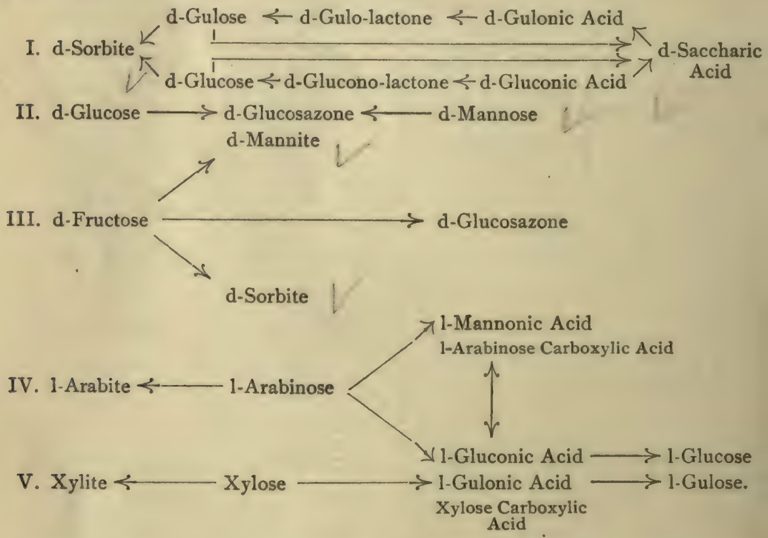
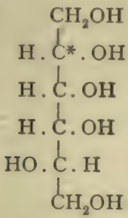


Diagram I shows that d-glucose or grape sugar and d-gulose yield the same d-saccharic acid. Hence it follows that d-saccharic acid and the d-sorbite corresponding to it can not have the formulas (1), (2), (3), (4) (p. 558), because it is only the hexites and saccharic acids, (5), (6), (7), (8), (9), (10), which yield two space isomeric aldohexoses each. The formulas (7) and (8) of the six space-formulas represent by virtue of intramolecular compensation optically inactive molecules, which therefore disappear for the optically active d-saccharic acid and d-sorbite.

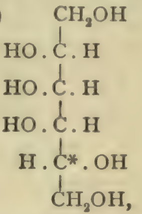
The fact that d-saccharic acid and d-mannosaccharic acid, d-gluconic and d-mannonic acids, d-glucose and d-mannose, d-sorbite and d-mannite, only differ by the varying arrangement of the univalent atoms or atomic groups with reference to the carbon atom, which in d-glucose and d-mannose is linked to the aldehydo-group, makes it possible to decide between the image formulas (5) and (6), (9) and (10); for d- and l-saccharic acid, d-mannose and d-glucose, yield the same osazone (diagram II above). l-Arabinose treated with hydrocyanic and hydrochloric acids gives rise to both l-mannonic or l-arabinose carboxylic acid, and l-gluconic acid (diagram IV above). The same relations which are observed with l-mannonic and l-gluconic acid prevail naturally with their image isomerides—d-mannonic acid and d-gluconic acid. A mixture of d-mannite and d-sorbite is obtained by the reduction of d-fructose. Assuming that d-sorbite and d-saccharic acid possessed the space-formulas (9) or (10) (p. 559):

(9)



$$\begin{array}{c}\mathrm{CH_2OH}\\ \mathrm{H.\overset{|}{C}^{*}.OH}\\ \mathrm{H.\overset{|}{C}.OH}\\ \mathrm{H.\overset{|}{C}.OH}\\ \mathrm{HO.\overset{|}{C}.H}\\ \mathrm{\overset{|}{C}H_2OH}\end{array}$$

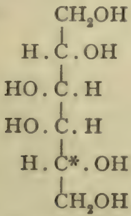
(10)



$$\begin{array}{c}\mathrm{CH_2OH}\\ \mathrm{HO.\overset{|}{C}.H}\\ \mathrm{HO.\overset{|}{C}.H}\\ \mathrm{HO.\overset{|}{C}.H}\\ \mathrm{H.\overset{|}{C}^{*}.OH}\\ \mathrm{\overset{|}{C}H_2OH,}\end{array}$$

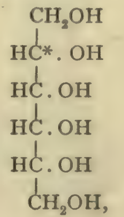
then d-mannite, and also d-mannosaccharic acid, would have the formulas (7) or (8):

(7)



$$\begin{array}{c}\mathrm{CH_2OH}\\ \mathrm{H.\overset{|}{C}.OH}\\ \mathrm{HO.\overset{|}{C}.H}\\ \mathrm{HO.\overset{|}{C}.H}\\ \mathrm{H.\overset{|}{C}^{*}.OH}\\ \mathrm{\overset{|}{C}H_2OH}\end{array}$$

(8)



$$\begin{array}{c}\mathrm{CH_2OH}\\ \mathrm{H\overset{|}{C}^{*}.OH}\\ \mathrm{H\overset{|}{C}.OH}\\ \mathrm{H\overset{|}{C}.OH}\\ \mathrm{H\overset{|}{C}.OH}\\ \mathrm{\overset{|}{C}H_2OH,}\end{array}$$

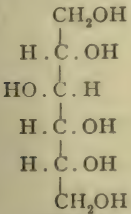
because only these formulas differ from (9) and (10) *exclusively* in the varying arrangement of the atoms or atom groups with reference to asymmetric carbon atoms, designated by little stars.

However, formulas (7) and (8) by intramolecular compensation give rise to inactive molecules, consequently can not give back the configuration of d-mannite and d-mannosaccharic acid.

Thus, for d-sorbite and l-sorbite, d-saccharic acid and l-saccharic acid there remain only formulas (5) and (6), from which (6) is arbitrarily selected for d-sorbite and d-saccharic acid, and (5) for l-sorbite and l-saccharic acid. When this has been done then all further arbitrary selection ceases; now the formulas for all optically active compounds connected experimentally with saccharic acid are regarded as established (B. 27, 3217). Hence, the space-formula (2) falls to d-mannite and d-mannosaccharic acid, and formula (1) to l-mannitol and l-mannosaccharic acid, which would also give formulas (2^1) and (1^1) to d- and l-mannonic acids.

The aldohexoses (7^1) and (8^1) (p. 558) correspond to d-sorbite and the saccharic acid with space-formula (6):

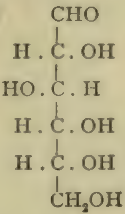
(6)



$$\begin{array}{c}\mathrm{CH_2OH}\\ \mathrm{H.\overset{|}{C}.OH}\\ \mathrm{HO.\overset{|}{C}.H}\\ \mathrm{H.\overset{|}{C}.OH}\\ \mathrm{H.\overset{|}{C}.OH}\\ \mathrm{\overset{|}{C}H_2OH}\end{array}$$

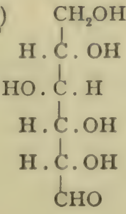
d-Sorbite
(d-Saccharic Acid).

(7^1)



$$\begin{array}{c}\mathrm{CHO}\\ \mathrm{H.\overset{|}{C}.OH}\\ \mathrm{HO.\overset{|}{C}.H}\\ \mathrm{H.\overset{|}{C}.OH}\\ \mathrm{H.\overset{|}{C}.OH}\\ \mathrm{\overset{|}{C}H_2OH}\end{array}$$

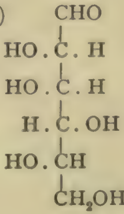
(8^1)



$$\begin{array}{c}\mathrm{CH_2OH}\\ \mathrm{H.\overset{|}{C}.OH}\\ \mathrm{HO.\overset{|}{C}.H}\\ \mathrm{H.\overset{|}{C}.OH}\\ \mathrm{H.\overset{|}{C}.OH}\\ \mathrm{\overset{|}{C}HO}\end{array}$$

or when rotated 180°

(8^1)



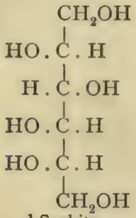
$$\begin{array}{c}\mathrm{CHO}\\ \mathrm{HO.\overset{|}{C}.H}\\ \mathrm{HO.\overset{|}{C}.H}\\ \mathrm{H.\overset{|}{C}.OH}\\ \mathrm{HO.\overset{|}{C}H}\\ \mathrm{\overset{|}{C}H_2OH}\end{array}$$

In order to obtain the aldehyde group at the top of the formula image, formula $(\underline{8}^1)$ must be turned 180°. This converts it into formula (8^1), and the succession of the atomic groups attached to the asymmetric carbon atom is naturally not altered.

The choice between formula (7^1) and (8^1) for d-glucose and d-gulose still remains. We are able to determine this if we can select out the space-formulas for the two image-isomerides—l-glucose and l-gulose. This is possible with a proper consideration of the genetic relation of the last two bodies with l-arabinose and xylose, as represented in diagrams IV and V (p. 560).

The formulas (5^1) and (6^1) of the aldohexoses correspond to the formula (5) of l-saccharic acid. $(\underline{6}^1)$ when rotated becomes (6^1):

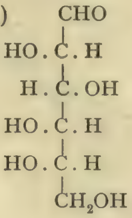
(5)



$$\begin{array}{c}\mathrm{CH_2OH}\\ \mathrm{HO.C.H}\\ \mathrm{H.C.OH}\\ \mathrm{HO.C.H}\\ \mathrm{HO.C.H}\\ \mathrm{CH_2OH}\end{array}$$

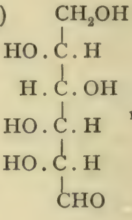
l-Sorbite
(l-Saccharic Acid).

(5^1)



$$\begin{array}{c}\mathrm{CHO}\\ \mathrm{HO.C.H}\\ \mathrm{H.C.OH}\\ \mathrm{HO.C.H}\\ \mathrm{HO.C.H}\\ \mathrm{CH_2OH}\end{array}$$

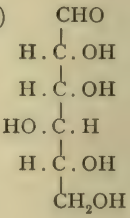
$(\underline{6}^1)$



$$\begin{array}{c}\mathrm{CH_2OH}\\ \mathrm{HO.C.H}\\ \mathrm{H.C.OH}\\ \mathrm{HO.C.H}\\ \mathrm{HO.C.H}\\ \mathrm{CHO}\end{array}$$

or when rotated 180°

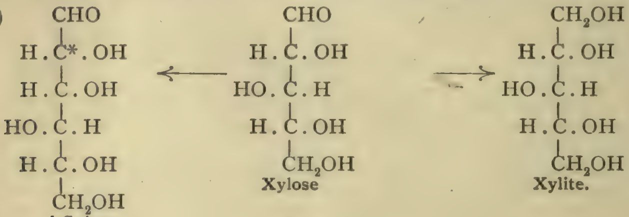
(6^1)



$$\begin{array}{c}\mathrm{CHO}\\ \mathrm{H.C.OH}\\ \mathrm{H.C.OH}\\ \mathrm{HO.C.H}\\ \mathrm{H.C.OH}\\ \mathrm{CH_2OH}\end{array}$$

Remembering that, according to diagram IV, page 560, it is possible to obtain d-glucose from l-arabinose, and, according to diagram V, l-gulose from xylose, then the pentoses mentioned must have the space-formulas which can be derived for formulas (5^1) and (6^1) by omitting the first C*-atom, becoming asymmetric in the synthesis:

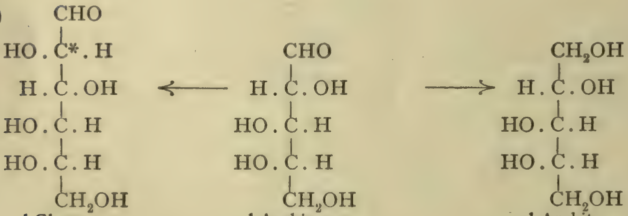
(6^1)



$$\begin{array}{ccccc}\mathrm{CHO} & & \mathrm{CHO} & & \mathrm{CH_2OH}\\ \mathrm{H.C^*.OH} & & \mathrm{H.C.OH} & & \mathrm{H.C.OH}\\ \mathrm{H.C.OH} & \longleftarrow & \mathrm{HO.C.H} & \longrightarrow & \mathrm{HO.C.H}\\ \mathrm{HO.C.H} & & \mathrm{H.C.OH} & & \mathrm{H.C.OH}\\ \mathrm{H.C.OH} & & \mathrm{CH_2OH} & & \mathrm{CH_2OH}\\ \mathrm{CH_2OH} & & & & \end{array}$$

l-Gulose Xylose Xylite.

(5^1)

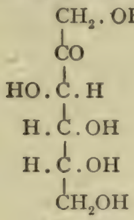


$$\begin{array}{ccccc}\mathrm{CHO} & & & & \\ \mathrm{HO.C^*.H} & & \mathrm{CHO} & & \mathrm{CH_2OH}\\ \mathrm{H.C.OH} & \longleftarrow & \mathrm{H.C.OH} & \longrightarrow & \mathrm{H.C.OH}\\ \mathrm{HO.C.H} & & \mathrm{HO.C.H} & & \mathrm{HO.C.H}\\ \mathrm{HO.C.H} & & \mathrm{HO.C.H} & & \mathrm{HO.C.H}\\ \mathrm{CH_2OH} & & \mathrm{CH_2OH} & & \mathrm{CH_2OH}\end{array}$$

l-Glucose l-Arabinose l-Arabite.

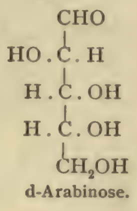
It is at once seen that the aldopentose corresponding to formula (6^1) must, by reduction, yield an inactive pentite-*xylite* (p. 534), —through an intramolecular compensation. Similarly, the pentose with formula (5^1) changes to an optically active pentite—l-*arabite* (p. 534). In this manner is fixed not only the configuration for xylite and xylose, l-arabite and l-arabinose, but it is also demonstrated that l-gulose, from xylose, has the formula (6^1), and l-glucose, synthesized from l-arabinose, the space-formula (5^1). (6^1) is the image-formula of space-formula (6^1). This, therefore, belongs to d-*gulose*. Formula (7^1) corresponds to space-formula (5^1), and hence it belongs to d-*glucose*. From all this it would follow that d and l-mannoses have formulas (2^1) and (1^1), which facts confirm: that d-glucose and d-mannose on the one hand, and l-glucose and l-mannose on the other, pass into the same glucosazone—*i. e.*, they differ only in the configuration at *one* asymmetric C-atom.

When it is remembered that d-fructose, by reduction, yields a mixture of d-mannite and d-sorbite, and d-glucosazone on treatment with phenylhydrazine, it will be recognized that both it and its corresponding d-arabinose must have the space-formulas:



$$\begin{array}{c} CH_2.OH \\ | \\ CO \\ | \\ HO.C.H \\ | \\ H.C.OH \\ | \\ H.C.OH \\ | \\ CH_2OH \end{array}$$

d-Fructose

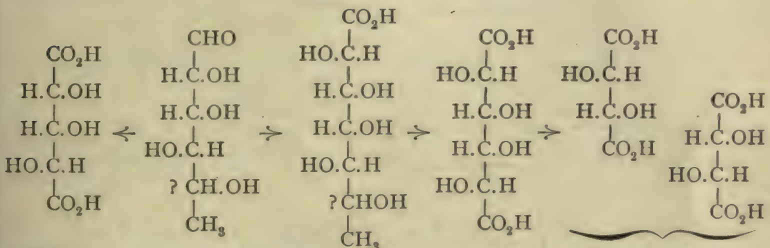


$$\begin{array}{c} CHO \\ | \\ HO.C.H \\ | \\ H.C.OH \\ | \\ H.C.OH \\ | \\ CH_2OH \end{array}$$

d-Arabinose.

DERIVATION OF THE CONFIGURATION OF d-TARTARIC ACID.

The configuration of d-tartaric acid is evident, according to E. Fischer, from its production in the oxidation of d-saccharic acid. The formula of the latter has been previously deduced above. It is in harmony, therefore, with its formation in the oxidation of methyl tetrose (p. 520), a decomposition product of rhamnose. The latter, when oxidized, passes into l-trioxyglutaric acid. The α-rhamnohexonic acid, obtained from the latter by the hydrocyanic acid addition, yields mucic acid on oxidation, and the latter, on similar treatment, changes to racemic acid. Assuming that the methyl group of rhamnose is eliminated in the oxidation of rhamnohexonic acid, we would have the following configuration-formula for rhamnose:

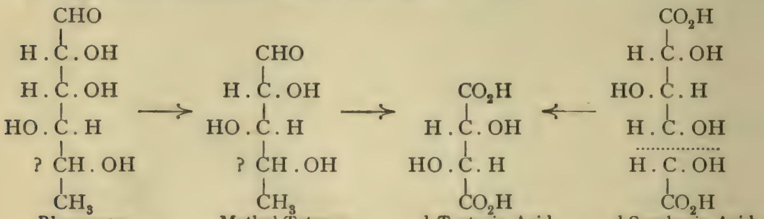


$$\begin{array}{c} CO_2H \\ | \\ H.C.OH \\ | \\ H.C.OH \\ | \\ HO.C.H \\ | \\ CO_2H \end{array} \leftarrow \begin{array}{c} CHO \\ | \\ H.C.OH \\ | \\ H.C.OH \\ | \\ HO.C.H \\ | \\ ?\ CH.OH \\ | \\ CH_3 \end{array} \rightarrow \begin{array}{c} CO_2H \\ | \\ HO.C.H \\ | \\ H.C.OH \\ | \\ H.C.OH \\ | \\ HO.C.H \\ | \\ ?\ CHOH \\ | \\ CH_3 \end{array} \rightarrow \begin{array}{c} CO_2H \\ | \\ HO.C.H \\ | \\ H.C.OH \\ | \\ H.C.OH \\ | \\ HO.C.H \\ | \\ CO_2H \end{array} \rightarrow \underbrace{\begin{array}{c} CO_2H \\ | \\ HO.C.H \\ | \\ H.C.OH \\ | \\ CO_2H \end{array} \quad \begin{array}{c} CO_2H \\ | \\ H.C.OH \\ | \\ HO.C.H \\ | \\ CO_2H \end{array}}$$

l-Trioxy-glutaric Acid — Rhamnose — α-Rhamnose-Carboxylic Acid — Mucic Acid — Racemic Acid.

This assumption has been proved through the behavior of the stereo-isomeric β-rhamnohexonic acid, which results on heating α-rhamnohexonic acid to 140° with pyridine. All experiences go to show that the two stereo-isomeric rhamnohexonic acids only differ in the arrangement or position of the carboxyl group in direct union with the asymmetric carbon atom. Had the methyl group not been split off in the oxidation, but merely changed to carboxyl, then α- and β-rhamnohexonic acids would have yielded the same mucic acid because the asymmetric C-atom linked to carboxyl in α- and β-rhamnohexonic acid, that caused the difference in the two acids, would have been oxidized to carboxyl. β-Rhamnohexonic acid, however, oxidizes to l-talomucic acid, which justifies the preceding assumption, and consequently proves the rhamnose configuration, even to the position of the asymmetric carbon atom linked to methyl.

Wohl's procedure permits of the conversion of rhamnose into methyl tetrose, which is oxidized to d-tartaric acid by nitric acid. Hence, we may suppose that here the methyl group is split off as in the case of the oxidation of rhamnose to l-trioxyglutaric acid, and of *a*-rhamnohexonic acid to mucic acid. This then demonstrates the configuration of d-tartaric acid (B. **29**, 1377):



Rhamnose Methyl Tetrose d-Tartaric Acid d-Saccharic Acid.

4. POLYOXYMONOCARBOXYLIC ACIDS.

A. PENTAOXYCARBOXYLIC ACIDS.

These acids are produced (1) by the further oxidation (by means of chlorine or bromine water) of the alcohols and aldoses corresponding to them; (2) by the reduction of the corresponding aldehydo-acids and lactones of dicarboxylic acids; synthetically, from the aldopentoses (arabinose, rhamnose, p. 536) by the aid of CNH, etc. This is analogous to the synthesis of glycollic acid from formaldehyde, and ethidene lactic acid from acetaldehyde:

$$CH_3.CHO \xrightarrow{CNH} CH_3.CH(OH)CN \xrightarrow[2H_2O]{HCl} CH_3.CH(OH).CO_2H$$

$$\underset{\text{l-Arabinose}}{CH_2.OH[CH.OH]_3CHO} \xrightarrow{CNH} \underset{\text{l-Glucononitrile}}{CH_2OH[CHOH]_3CH(OH)CN} \xrightarrow[2H_2O]{HCl} CH_2OH[CHOH]_3CH(OH)CO_2H$$

l-Gluconic Acid
l-Arabinose Carboxylic Acid.

Deportment.—Being γ- and δ-oxy-derivatives, nearly all of these acids are very unstable when in a free condition. They lose water readily and pass into *lactones* (p. 342):

$$C_6H_{12}O_7 \xrightarrow{-H_2O} C_6H_{10}O_6.$$

When acted upon in acid solution by sodium amalgam, these lactones (not the acids) reabsorb two atoms of hydrogen, and are converted into the corresponding aldohexoses (E. Fischer):

$$\underset{\text{d-Glucono-lactone}}{C_6H_{10}O_6} \xrightarrow{2H} \underset{\text{d-Glucose.}}{C_6H_{12}O_6.}$$

These acids, when acted upon with phenylhydrazine, form characteristic crystalline *phenylhydrazides*, $C_6H_{11}O_6 . N_2H_2 . C_6H_5$ (B. **22**, 2728). They are resolved into their components when boiled with alkalies. They are distinguished from the hydrazones of the aldehydes and ketones by the *reddish-violet* coloration produced upon mixing them with concentrated sulphuric acid and a drop of ferric chloride.

Heated to 130–150° with quinoline or pyridine a geometric rearrangement ensues, which is, however, restricted to the asymmetric carbon atom in union with the carboxyl. It is a reversible reaction, and therefore yields a mixture of both stereo-isomerides, *e. g.* (B. **27**, 3193):

$$\begin{tikzcd}
\text{d- and l-Gluconic Acid} \arrow[r, leftrightarrow] & \text{d- and l-Mannonic Acid.} \\
\text{l-Gulonic Acid} \arrow[r, leftrightarrow] & \text{l-Idonic Acid.} \\
\text{d-Galactonic Acid} \arrow[r, leftrightarrow] & \text{d-Talonic Acid.}
\end{tikzcd}$$

These acids are reduced to lactones of the γ-monoxycarboxylic acids (p. 345), if they are heated with hydriodic acid and phosphorus.

Isomerism.—Spacial isomerides of pentaoxy-n-caproic acid are as numerous, according to theory, as the aldohexoses (p. 558), *i. e.*, sixteen optically active and eight [d + l] modifications, which are inactive.

Mannonic Acid, $C_5H_6(OH)_5 . CO_2H$. The syrup-like acids—d-, l-, and [d + l]-mannonic acid—yield d-, l-, and [d + l]-*mannosaccharic acid* on oxidation (p. 569). They change to lactones on evaporating their solutions, which by further reduction yield d-*mannite*, l-*mannite*, and [d + l]-*mannite*. [d + l]-*Mannite is identical with α-acrite, the reduction product of synthetic α-acrose* or [d + l]-fructose. As [d + l]-mannite or α-acrite, when oxidized, yields [d + l]-mannose, and the latter by similar treatment becomes [d + l]-mannonic acid, which can be split into d-mannonic acid and l-mannonic acid, we realize through these reactions the complete synthesis of all bodies of the mannite series (p. 554):

$$\begin{tikzcd}
 & \text{d-Mannite} & \text{d-Mannose} \arrow[l] & \text{d-Mannono-lactone} \arrow[l] & \\
 & & & \text{d-Mannonic Acid} \arrow[r] & \text{Mannosaccharic Acid} \\
\text{α-Acrose [d+l] Fructose} \arrow[r] & \text{α-Acrite [d+l] Mannite} & \text{[d+l] Mannose} \arrow[l] & \text{[d+l] Mannonic Acid} \arrow[l] \arrow[r] & \text{[d+l] Mannosaccharic Acid} \\
 & & & \text{l-Mannonic Acid} \arrow[r] & \text{l-Mannosaccharic Acid} \\
 & \text{l-Mannite} & \text{l-Mannose} \arrow[l] & \text{l-Mannono-lactone.} \arrow[l] &
\end{tikzcd}$$

d-Mannono-lactone, $C_6H_{10}O_6$,	m.p. 149–153°	$[\alpha]_D = + 53.8°$
l-Mannono-lactone,	“ 140–150°	$[\alpha]_D = + 54.8°$
[d + l] Mannono-lactone, $(C_6H_{10}O_6)_2$,	“ 149–155°.	

d- and l-*Mannonophenylhydrazide*, $C_6H_{11}O_6(N_2H_2 . C_6H_5)$, melts at 214–216°.

[d + l] *Mannonophenylhydrazide* melts about 230° when it is rapidly heated. The hydrazides are converted into the acids on boiling with baryta water (B. **22**, 3221). This reaction is well adapted for the purification of the acids.

A very important feature is that *a partial conversion of d- and l-mannonic acid into d- and l- gluconic acids occurs on heating the former to 140° with quinoline.* The last two acids, subjected to the same treatment, change in part to d- and l-mannonic acids.

This method of preparing d- and l-gluconic acids shows the genetic connection existing between d- and l-glucose and the mannite series, and thereby renders possible the synthesis of grape sugar.

The formation of l-mannonic acid or l-arabinose-carboxylic acid (together with l-gluconic acid) from l-arabinose by means of hydrocyanic acid constitutes one of the transitions which allows of the synthesis of aldohexoses from aldopentoses:

$$\text{l-Arabinose}\left\{\begin{array}{l}\text{l-Mannonic Acid} \longrightarrow \text{l-Mannono-lactone} \longrightarrow \text{l-Mannose}\\ \text{l-Arabinose Carboxylic Acid}\\ \text{l-Gluconic Acid} \longrightarrow \text{l-Glucono-lactone} \longrightarrow \text{l-Glucose.}\end{array}\right.$$

Gluconic Acid, $CH_2OH(CHOH)_4CO_2H$, is known in the d-, l-, and [d + l]-modifications (B. **23**, 801, 2624; **24**, 1840).

1. The lactones of these three acids change to d-, l-, and [d + l]-glucose on reduction.
2. By oxidation they become d-, l-, and [d + l] saccharic acids.
3. When heated to 140° with quinoline they change in part to d-, l-, and [d + l] mannonic acids (p. 566). Conversely, d-, l-, and [d + l] gluconic acids are won by the same treatment from d-, l-, and [d + l] mannonic acids.

The d- and l-phenylhydrazides, $C_6H_{11}O_6(N_2H_2 . C_6H_5)$, melt about 200° when they are rapidly heated, while the [d + l] phenylhydrazide melts at 190°.

d-**Gluconic Acid**, *Dextronic Acid, Maltonic Acid*, is formed by the oxidation of dextrose, cane sugar, dextrine, starch, and maltose with chlorine or bromine water, and is most readily obtained from glucose (B. **17**, 1298) as well as from d-mannonic acid. Gluconic acid forms a syrup which, when evaporated or upon standing, changes in part to its crystalline lactone, $C_6H_{10}O_6$, melting at 130–135°. Sodium amalgam reduces it to d-*glucose* or *grape sugar* (B. **23**, 804). Its barium salt crystallizes with three molecules of water, the calcium salt with one. The acid is dextro-rotatory, but does not reduce Fehling's solution.

Pentacetylglucononitrile, $C_5H_6(O . C_2H_3O)_5CN$ (B. **26**, 730). *Dimethylene Gluconic Acid*, $C_6H_8O_7(: CH_2)_2$, from d-gluconic acid and formaldehyde, melts at 220° (A. **292**, 31).

l-Gluconic acid is formed (1) from l-mannonic acid (p. 566), and (2) together with l-mannonic acid from l-arabinose by aid of CNH.

[d + l] **Gluconic Acid** is formed upon evaporating the aqueous solution of a mixture of d- and l-gluconic acids. Its calcium salt dissolves with difficulty. It is obtained like calcium racemate by mixing solutions of d- and l-gluconates of calcium.

Gulonic Acid, $CH_2OH[CHOH]_4CO_2H$, is known in three forms, which become d-, l-, and [d + l] saccharic acids (p. 569) when they are oxidized. The reduction of their lactones produces d-, l-, and [d + l] *guloses* (p. 551). d-*Gulonic acid* is obtained by reduction of both glucuronic acid (p. 568) and d-saccharic acid. The *lactone* melts at 180–181°; the *phenylhydrazide* at 147–148° (B. **24**, 526). l-*Gulonic acid*, xylose carboxylic acid, results when xylose is acted upon with CNH. This reaction unites also the aldopentoses with the aldohexoses. l-Idonic acid is produced simultaneously, and when heated with pyridine changes partially to l-gulonic acid. l-*Gulono-lactone* melts at 185°. The *phenylhydrazide* melts at 147–149° (B. **23**, 2628; **24**, 528). [d + l] *Gulonic Acid* readily changes into its lactone, which by crystallization splits into d- and l-gulono-lactone. Calcium [d + l] gulonate dissolves with more difficulty than calcium d- and l-gulonate. The *phenylhydrazide* melts at 153–155° (B. **25**, 1025).

l-**Idonic Acid** is formed together with l-gulonic acid from xylose, and is separated by means of its brucine salt from the mother liquor of l-gulono-lactone. Heated with pyridine to 140°, it changes in part to l-gulonic acid, and *vice versâ*. l-Idose is its reduction product (p. 551). d-*Idonic Acid*, obtained from d-gulonic acid by means of pyridine, yields d-idose on reduction (B. **28**, 1975).

Galactonic Acid, $CH_2OH[CHOH]_4CO_2H$, is known in three modifications. [d + l] *Galactonic Acid* results in the reduction of ethyl mucic ester and also of the lactone of mucic acid. Its [d + l] *lactone* melts at 122–125°. Its *phenylhydrazide* melts at 205°. This acid can be resolved by means of its strychnine salt into the l-salt, which is more easily soluble in alcohol, and the d-salt, which dissolves with more difficulty (B. **25**, 1256). l-*Galactonic Acid* resembles in a remarkable degree the well-known—

d-**Galactonic Acid**, *Lactonic Acid*, $CH_2OH[CHOH]_4CO_2H$, which is produced from milk sugar, d-galactose, and gum arabic by the action of bromine water. It can be converted into d-talonic acid, and then be prepared from the latter. It crystallizes, and prolonged heating to 100° converts it into the corresponding lactone, $C_6H_{10}O_6$, melting at 90–92°, which combines with water to $C_6H_{10}O_6 + H_2O$, melting at 64–65° (A. **271**, 83). *Calcium Salt*, $(C_6H_{11}O_7)_2Ca + 5H_2O$. Its *phenylhydrazide* melts at 200–205°. Sodium amalgam causes the lactone to revert to d-galactose. It yields mucic acid on oxidation with nitric acid. The *amide* melts at 172°. The *anilide* melts at 210° (B. **28**, R. 606).

d-**Talonic Acid**, $CH_2CH[CHOH]_4CO_2H$, results together with oxymethylene pyromucic acid on heating d-galactonic acid with pyridine or quinoline to 140–150°. Conversely, d-galactonic acid is obtained from d-talonic acid by the same treatment (B. **27**, 1526). Reduction changes it to d-talose (p. 551).

Chitonic Acid is produced when HCl-glucosamine (p. 550) is changed to chitose by means of silver nitrite, and this non-isolated intermediate product is afterwards oxidized with bromine water (B. **27**, 140).

α-**Rhamnose-carboxylic Acid**, $CH_3(CH.OH)_4.CH\!<\!\begin{smallmatrix}OH\\CO_2H\end{smallmatrix}$, is made from rhamnose by action of CNH, etc. The *lactone*, $C_7H_{12}O_6$, melts at 162–168° (B. **21**, 2173). Its *phenylhydrazide*, $C_7H_{13}O_6.N_2H_2.C_6H_5$, melts about 210° (B. **22**, 2733).

When the acid is heated with hydriodic acid and phosphorus, it is reduced to normal heptylic acid. Sodium amalgam converts the lactone into *methylhexose* (B. **23**, 936). Mucic acid is its oxidation product (B. **27**, 384). Heated to 150–155° with pyridine, it is partly changed to β-*rhamnose-carboxylic acid*. The *lactone* of the latter melts at 134–138°, and the *phenylhydrazide* at 170°. When oxidized the β-acid is converted into l-talo-mucic acid (p. 571).

B. ALDOHEXOSE CARBOXYLIC ACIDS, HEXAOXYMONOCARBOXYLIC ACIDS.

Acids of this kind have been obtained from d-glucose, d-mannose, d galactose, and d-fructose by the addition of hydrocyanic acid, and the subsequent saponification of the nitrile with hydrochloric acid.

(1) **Mannoheptonic Acid** is known in three modifications:

d-**Mannose-carboxylic Acid**, d-*Mannoheptonic Acid*, $CH_2OH.[CHOH]_5.CO_2H$, is obtained from d-mannose (A. **272**, 197). Its *phenylhydrazide* (see above) melts about 220° with decomposition. Its *lactone* melts at 148–150°. Sodium amalgam reduces the lactone to d-mannoheptose, $C_7H_{14}O_7$, and then to the heptahydric alcohol perseïte, $C_7H_{16}O_7$ (B. **23**, 936, 2226). Hydriodic acid reduces the acid to heptolactone and heptylic acid (see above and B. **22**, 370). When oxidized it yields l-pentoxypimelic acid (A. **272**, 194). l-*Mannose Carboxylic Acid* is obtained from l-mannose. Its *phenylhydrazide* melts about 220°; its *lactone* at 153–154°. [d + l] Mannose carboxylic acid is formed from d- and l-mannose carboxylic acid, as well as from [d + l] mannose (A. **272**, 184).

(2) *a*, d-**Glucose-carboxylic Acid,** *a*, d-*Glucoheptonic Acid*, $CH_2OH[CHOH]_5$-CO_2H, is formed (1) together with the β-acid from d-glucose; (2) on heating the β-acid to 140° with pyridine; (3) by the hydrolysis of lactose- and maltose-carboxylic acids (pp. 575, 576) (A. **272**, 200). The lactone melts about 145°. Hydriodic acid reduces it to heptolactone and normal heptylic acid. Sodium amalgam reduces the lactone to *dextroheptose* (d-glucoheptose). The *a*,d-*phenylhydrazide* melts at 171° (B. **19**, 1916; **23**, 936; space-formula, A. **270**, 65). i-Pentaoxypimelic acid (p. 571) is formed when dextrose-carboxylic acid is oxidized. β, d-*Glucose-carboxylic Acid* is formed together with the *a*-acid from glucose. The *phenylhydrazide* melts at 150–152°. Its *lactone* melts at 151–152°, and yields β, d-glucoheptose on reduction.

a, d-**Galactose-carboxylic Acid,** *a*-*Galaheptonic Acid*, $CH_2OH[CHOH]_5CO_2H$, is produced together with *β-galaheptonic acid* from galactose. The acid melts at 145°, and passes into its *lactone*, melting at 150°. Sodium amalgam changes it into *a*-gala-heptose (p. 553). When oxidized it yields carboxy-d-galactonic acid (p. 571) (A. **288**, 39).

d-**Fructose-carboxylic Acid,** $CH_2OH.[CHOH]_3C(OH)(CO_2H)CH_2OH$, is obtained from fructose or lævulose by the action of hydrocyanic acid. It yields tetrahydroxybutane tricarboxylic acid when it is oxidized. Its *lactone* melts at 130°, and when reduced with sodium amalgam two aldoheptoses with branched C-chains result (B. **23**, 937). Reduction with hydriodic acid forms heptolactone and heptylic acid, $C_7H_{14}O_2$. The latter is identical with methyl-normal butyl acetic acid (p. 249). Hence it is evident that *lævulose* is a *ketone-alcohol* (Kiliani, B. **19**, 1914; **23**, 451; **24**, 348).

C. ALDOHEPTOSE CARBOXYLIC ACIDS, HEPTAOXYCARBOXYLIC ACIDS.

d-**Manno-octonic Acid,** $CH_2OH.[CHOH]_6CO_2H$, has been obtained from d-mannoheptose. Its *hydrazide* melts at 243°. The *lactone* has a neutral reaction, a sweet taste, and melts about 168°. By reduction it forms d-mannoctose (p. 553). *a*- and *β-Gluco-octono-lactone* melt at 145° and 186° (A. **270**, 93). *a-Gala-octono-lactone*, from *a*-galaheptose (A. **288**, 149), melts at 220–223°.

D. ALDO-OCTOSE CARBOXYLIC ACIDS, OCTO-OXYCARBOXYLIC ACIDS.

d-**Manno-nononic Acid,** $CH_2OH[CHOH]_7CO_2H$, has been obtained from d-manno-octose. Its *hydrazide* melts about 254°. Its *lactone* melts at 176°. When reduced it forms d-**manno-nonose.**

5. TETRAOXY- AND PENTAOXYALDEHYDE ACIDS.

d-**Glucuronic Acid,** $CHO.(CH.OH)_4.CO_2H$, is obtained by decomposing euxanthic acid (see this) on boiling with dilute sulphuric acid. Various glucoside-like compounds of glucuronic acid with camphor, borneol, chloral, phenol, and different other bodies (B. **19**, 2919, R. 762) occur in urine after the introduction of these compounds into the animal organism. In this change the substances mentioned combine with the aldehyde group of grape sugar, the primary alcohol group of which is then oxidized. Boiling acids decompose them into their components. Glucuronic acid is a syrup, which rapidly passes into the lactone $C_6H_8O_6$ on warming. The latter consists of large plates, of sweet taste, melting at 175–178° C. Bromine water oxidizes it to saccharic acid. It also appears that when saccharic acid is reduced glucuronic acid results (B. **23**, 937), and by reduction d-gluconic acid is formed (B. **24**, 525). The position of the aldehyde group in camphor-glucuronic acid and euxanthic acid is fully established. *Urochloralic Acid*, $C_8H_{11}Cl_3O_7$, melting at 142°, decomposes with water absorption on boiling with dilute hydrochloric or sulphuric acid into glucuronic acid and trichlorethyl alcohol (p. 125). *Urobutylchloralic Acid*, $C_{10}H_{15}Cl_3O_7$, decomposes, like the preceding body, into glucuronic acid and $\alpha\alpha\beta$-trichlorbutyl alcohol (p. 126).

Aldehydo-galactonic Acid, $COH\,.\,[CHOH]_5CO_2H$, is obtained from d-galactose carboxylic acid, and may be converted into carboxy-galactonic acid (p. 571).

6. POLYOXYDICARBOXYLIC ACIDS.

A. TETRAOXYDICARBOXYLIC ACIDS.

These are obtained by the oxidation of various carbohydrates with nitric acid, and are readily prepared from the corresponding monocarboxylic acids upon oxidation with nitric acid. Mannosaccharic acid, the saccharic acids, and the mucic acids are the most important representatives of the series. Gluconic acid yields saccharic acid, galactonic acid mucic acid, and mannonic acid mannosaccharic acid. Their lactones, by very careful reduction, can be converted into aldehyde oxycarboxylic acids and oxymonocarboxylic acids. When reduced by HI and phosphorus the preceding acids are converted into normal adipic acid, $C_4H_8(CO_2H)_2$; hence all of them must be considered as normal space-isomeric tetraoxyadipic acids. Theoretically, ten simple and four double modifications are possible. All the tetraoxyadipic acids, when heated with hydrochloric or hydrobromic acid, change more or less readily to dehydromucic acid (B. **24**, 2140).

(1) **Mannosaccharic Acid,** $CO_2H[CHOH]_4CO_2H$, is known in three modifications (space-formula, p. 558), which pass into double lactones when they are liberated from their salts. They also result upon oxidizing the three mannonic acids with nitric acid (p. 565).

[d + l] *Mannosaccharo-lactone*, $C_6H_6O_6$, melts with decomposition at 190°. It is formed by the union of d- and l-mannosaccharo-lactone, and also from [d + l] manno-lactone. Its *diamide* melts at 183–185°. Its *dihydrazide* melts at 220–225° (B. **24**, 545).

d-*Mannosaccharo-lactone*, $C_6H_6O_6 + 2H_2O$, melts with decomposition, when anhydrous, at 180–192°. It is produced when d-mannite, d-mannose, and d mannonic acid are oxidized with nitric acid. Its *diamide* melts at 189°. Its *dihydrazide* melts at 212° (B. **24**, 544). *Metasaccharic Acid*, $C_6H_6O_6 + 2H_2O$, melts at 68°; when anhydrous, at 180°. It is produced when l-mannonic acid and the lactone of l-arabinose carboxylic acid are oxidized (B. **20**, 341, 2713). Its *diamide* melts at 189–190°. Its *dihydrazide* melts at 212–213°. *Diactyl-l-mannosaccharo lactone* melts at 155° (B. **21**, 1422; **22**, 525; **24**, 541).

(2) d- and l-**Idosaccharic Acids** are syrups. They are obtained by oxidizing the corresponding idonic acid (p. 567).

(3) **Saccharic Acid,** $CO_2H[CHOH]_4CO_2H$, exists in three modifications (space-formulas, p. 558); of these the d-saccharic acid is ordinary saccharic acid.

[d + l]-*Saccharic Acid* is formed by the oxidation of [d + l]-gluconic acid. Its monopotassium salt is formed on mixing solutions of equal quantities of the d- and l-salt. Its *dihydrazide* melts at 210° (B. **23**, 2622).

Ordinary, or d-saccharic acid, results in the oxidation of cane sugar (B. **21**, R. 472), d-glucose (grape sugar), d-gluconic acid, and many carbohydrates with nitric acid; also from the action of bromine water upon glucuronic acid.

It forms a deliquescent mass, readily soluble in alcohol. If the pure, syrupy acid be allowed to stand for some time, it changes to its crystalline lactonic acid, $C_6H_8O_7$, which melts at 130–132°. It changes to glucuronic acid when reduced with sodium amalgam. Hydriodic acid reduces it to adipic acid. When oxidized with nitric acid, dextro-tartaric acid (B. **27**, 396) and oxalic acid are formed.

The *primary potassium salt*, $C_6H_9KO_8$, and the *ammonium salt*, $C_6H_9(NH_4)O_8$, dissolve with difficulty in cold water. The *diethyl ester* is crystalline. The *amide* is a white powder. The *tetra-acetate* melts at 61°. Acetyl chloride, acting upon free saccharic acid, converts it into the *lactone of diacetyl-saccharic acid*, $C_6H_4(O.C_2H_3O)_2O_4$, melting at 188°. *Monomethylene Saccharic Acid* (A. **292**, 40). Its *diamide* is a white powder.

Its *dihydrazide* melts at 210° with decomposition (B. **21**, R. 186).

l-*Saccharic acid* is obtained upon oxidizing l-gluconic acid with nitric acid. It is quite similar to d-saccharic acid, but is lævorotatory. It also forms a *dihydrazide*, melting at 214°.

(4) **Mucic Acid**, $CO_2H[CHOH]_4CO_2H$, *Acidum mucicum*, corresponds in constitution to dulcitol. It has the space-formula No. 7 (p. 559). This is also evident from its yielding racemic acid on oxidation, and from the fact that it is formed when *α*-rhamnose carboxylic acid is oxidized (p. 567; B. **27**, 396).

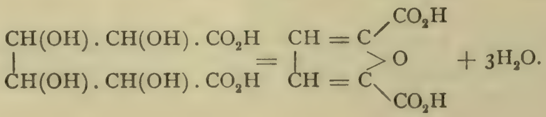
It is also obtained in the oxidation of dulcitol, milk-sugar (Preparation, A. **227**, 224), d- and l-galactose, d- and l-galactonic acid, and nearly all the gum varieties.

It is a white crystalline powder, almost insoluble in cold water and alcohol. It melts at 210° with decomposition. When boiled for some time with water it passes into a readily soluble lactonic acid, $C_6H_8O_7$, formerly designated *paramucic acid*, d-saccharo-lactonic acid (p. 569; B. **24**, 2141).

Reduction changes this muci-lactonic acid into [d + l]-galactonic acid (p. 567; B. **25**, 1247).

Mucic acid heated to 140° with pyridine becomes *allomucic acid*, from which it can be reformed under similar conditions.

The ready conversion of mucic acid into furfurane derivatives is rather remarkable. Digestion with fuming hydrochloric or hydrobromic acid changes it to furfurane dicarboxylic acid (*dehydromucic acid*):



When mucic acid is heated alone it splits off carbon dioxide and becomes furfurane monocarboxylic acid (*pyromucic acid*):

$$C_4H_4(OH)_4(CO_2H)_2 = C_4H_3O\,.\,CO_2H + 3H_2O + CO_2.$$

Heated with barium sulphide it passes in like manner into α-thiophene carboxylic acid (B. **18**, 457).

Pyrrol, NH_3, CO_2, and water are produced when the diammonium salt is heated:

$$C_6H_8(NH_4)_2O_8 = C_4H_4NH + NH_3 + 2CO_2 + 4H_2O.$$

The *neutral potassium salt* and *ammonium salt*, $C_6H_8(NH_4)_2O_8$, crystallize well and dissolve with difficulty in cold water; the *primary salts* dissolve readily. The *silver salt*, $C_6H_8Ag_2O_8$, is an insoluble precipitate.

The *diethyl ester* melts at 158°. The *tetra-acetate* melts at 177° (B. **21**, R. 186).

See p. 467 for the action of PCl_5 upon mucic acid.

(5) **Allomucic Acid**, $C_6H_{10}O_8$, melts at 166–171°, is optically inactive, and more soluble than mucic acid, from which it is obtained on heating with pyridine, and into which it also passes (see mucic acid) (B. **24**, 2136).

(6) **Talomucic Acid**, $CO_2H[CHOH]_4CO_2H$, is known in two space-isomeric modifications:

d-*Talomucic Acid*, melting with decomposition at 158°, and resulting from the oxidation of d-talonic acid (B. **24**, 3625).

l-*Talomucic Acid*, prepared by oxidizing β-rhamnose carboxylic acid (p. 567) (B. **27**, 384).

(7) **Isosaccharic Acid**, $CO_2H\,.\,\overbrace{CH\,.\,CH(OH)OCH(OH)\,.\,CH}\,.\,CO_2H$, results from HCl-glucosamine (p. 550) upon oxidizing it with nitric acid (B. **19**, 1258). It melts at 185°. Its solution is dextrorotatory; $(\alpha)_D = +46.1°$. The acid itself and some of its derivatives must be regarded as compounds of tetrahydro-furfurane. This is evident from the constitution formula of the acid. Other derivatives should be referred to isosaccharic acid + H_2O—that is, to tetraoxyadipic acid, and they are described as derivatives of noriso-saccharic acid; for example, the *diethyl ester*, $C_6H_8O_8(C_2H_5)_2$, melting at 73°, which changes in the desiccator to the *diethyl ester* of isosaccharic acid, $C_6H_6O_7(C_2H_5)_2$, melting at 101°.

The *diacetyl isosaccharic ester* melts at 49° (B. **27**, 118).

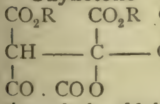
B. PENTAOXYDICARBOXYLIC ACIDS.

Pentaoxypimelic Acid, *Heptanpentol diacid*, $CO_2H\,.\,[CH\,.\,OH]_5CO_2H$, is produced in the oxidation of glucose carboxylic acid with nitric acid. The *lactone* is crystalline, and melts at 143° (B. **19**, 1917).

α-**Carboxy-galactonic Acid**, α-*Galaheptanpentol Diacid*, $CO_2H[CHOH]_5CO_2H$, is formed in the oxidation of galactose-carboxylic acid with nitric acid. It dissolves with difficulty in water, crystallizes in plates, and melts at 171° with decomposition.

β-**Galaheptanpentol Diacid**, from β-galaheptonic acid and nitric acid, is a syrup (A. **288**, 155).

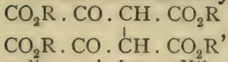
Oxyketone Tetracarboxylic Acids: *Ethyl Oxalo-citro-lactone Ester*,



$$\begin{array}{ccccc} CO_2R & & CO_2R & & CO_2R \\ | & & | & & | \\ CH & — & C & — & CH_2 \\ | & & | & & \\ CO & . & CO\,O & & \end{array}$$

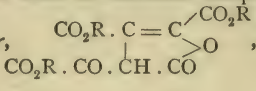
, boiling at 210° (30 mm.), is obtained from oxalacetic ester through the aldol condensation and lactone formation (A. **295**, 347).

Diketo-tetracarboxylic Acids: Ethyl Dioxalosuccinic Ester,



$$\begin{array}{l} CO_2R\,.\,CO\,.\,CH\,.\,CO_2R \\ \qquad\qquad\;\, | \\ CO_2R\,.\,CO\,.\,CH\,.\,CO_2R \end{array},$$

results on condensing succinic ester and oxalic ester with sodium ethylate. When distilled under greatly reduced pressure it loses carbon monoxide, and becomes ethane tetracarboxylic ester. When it is separated by means of sulphuric acid from its disodium compound it changes to *Ethyl Dioxalo-succino-lactone Ester*,



$$\begin{array}{l} \qquad CO_2R\,.\,C = C\begin{smallmatrix} \diagup CO_2R \\ >O \end{smallmatrix} \\ \qquad\qquad\quad | \\ CO_2R\,.\,CO\,.\,CH\,.\,CO \end{array}$$

, melting at 89° (A. **285**, 11).

CARBOHYDRATES.*

This term is applied to a large class of compounds, including the natural sugars, widely distributed in nature. They contain six, or a multiple of six carbon atoms. The ratio of their hydrogen and oxygen atoms is the same as that of these elements in water.

Most of the carbohydrates have their origin in plants, although some are produced in the animal organism. Those which occur in the vegetable kingdom meet with the most extensive application.

Carbohydrates serve for the preparation of alcoholic drinks (p. 122). Starch is the chief ingredient of flour from which bread, the most important nutrient, is made. It is found stored up in potatoes and grain fruits. Cellulose, related to it, is the principal constituent of wood, and is applied in paper-making and for the production of explosives. The carbohydrates in conjunction with the albuminoids constitute the most important compounds for man.

Their molecular magnitude is the basis of their arrangement into these classes:

Monoses, or *Monosaccharides*,
Saccharobioses, or *Disaccharides*,
Saccharotrioses, or *Trisaccharides*,
Polysaccharides.

The monosaccharides, including grape sugar and fruit sugar, have already been discussed in connection with the hexahydric alcohols, of which they are the first oxidation products (p. 542).

Nearly all of the naturally occurring carbohydrates are *optically active;* their solutions rotate the plane of polarization. The specific rotatory power is not only influenced by the temperature and concentration of their solutions, but very frequently also by the presence of inactive substances (B. **21**, 2588, 2599). Some represen-

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* "Kohlenhydrate," von B. Tollens. "Die Chemie der Zuckerarten," von E. O. von Lippmann, II. Auflage, 1895. "Die Chemie der Kohlenhydrate und ihre Bedeutung für die Physiologie," von E. Fischer, 1894.

tatives also manifest the phenomena of birotation and semirotation (p. 549). Constant rotation is generally attained by heating the solutions for a brief period. The determination of the gyratory power of the carbohydrates by means of the saccharimeter serves to ascertain their purity, or for the determination of their amount when dissolved: optical sugar test, saccharimetry (p. 574).

A. DISACCHARIDES, SACCHAROBIOSES.

Disaccharides, consisting of two molecules of glucoses or monoses (p. 549), hence termed *bioses*, have up to the present only been known with the hexoses, $C_6H_{12}O_6$. Their formula would therefore be $C_{12}H_{22}O_{11}$. By the absorption of water they are resolved into two molecules of the hexoses:

$$C_{12}H_{12}O_{11} + H_2O = 2C_6H_{12}O_6.$$

This reaction is known as hydrolytic decomposition or *hydrolysis*. The higher carbohydrates are also capable of undergoing this change.

The constitution of the disaccharides indicates that they are ether-like anhydrides of the hexoses. The union is effected through the alcohol or aldehyde groups. Milk sugar and maltose also contain the aldose group, CH(OH) . CHO, because they reduce Fehling's solution upon boiling, form osazones with phenylhydrazine, and when oxidized with bromine water yield monobasic acids, $C_{12}H_{22}O_{12}$, lacto- and maltobionic acid (p. 576) (B. **21**, 2633; **22**, 361).

Cane sugar does not show reducing power and does not yield an osazone. The reducing groups (of grape sugar and fruit sugar) appear to be combined in this compound.

The osazones of some of these sugars split off glyoxalosazone when treated with alkalies (B. **29**, R. 991).

Unorganized *ferments*, such as *diastase* and *synaptase* or *emulsin* (contained in sweet and bitter almonds), acting upon the saccharides produce hydrolysis. Invertin (changing a dextro-gyratory sugar solution into lævo-rotatory *invert sugar*), ptyalin (the ferment of saliva), trypsin, pepsin, and other animal secretions exert a like action.

When the di- and poly-saccharides are heated with water and a little acid they undergo hydrolysis. Its rapidity, according to Ostwald, bears a close relation to the affinity of the acids (Jour. pr. Chem. (2), **31**, 307). Certain inorganic salts, and also glycerol, are capable of inverting cane sugar (B. **29**, R. 950; **27**, R. 574).

Prolonged heating with acids causes *reversion;* the glucoses (especially fructose) undergo a retrogressive condensation to dextrine-like substances (B. **23**, 2094).

Cane Sugar, *Saccharose*, *Saccharobiose*, $C_{12}H_{22}O_{11}$, the most important of the sugars, occurs in the juice of many plants, chiefly in sugar cane (*Saccharum officinarum*) (20 per cent. of the juice), in some varieties of maple, and in beet-roots (*Beta maritima*) (10–20 per cent.), from which it is prepared on a commercial scale; and also in the seeds of some plants. While the hexoses occur mainly in fruits, cane sugar is usually contained in the stalks of plants.

Historical.—Sugar has been obtained from sugar cane from the earliest times. In the middle ages sugar cane was a rarity in Germany; it was only after the discovery of America that it was gradually introduced as a sweetening agent. In 1747 Marggraf,* in Berlin, discovered cane sugar in beet-roots; his observations became the basis of the beet-sugar industry.

In 1801 Achard, in Silesia, erected the first beet-sugar factory. The continental blockade forced by Napoleon I hastened the development of the new industry, which during the last fifty years has attained a constantly increasing importance in Germany. This country produces about one-fourth of the total sugar yield of the world. In the year 1891–92, 403 factories consumed 9,488,002 tons (1 ton = 1000 kilos) of beets, which were obtained from 164,774 hectares, and gave to commerce 1,144,368 tons of beet-sugar, from which the country gathered 72,000,000 M. revenue.†

Technical Preparation.‡—The cane sugar is best removed from the cane and from the finely divided beets by the diffusion process. The saccharine juice diffuses through the cell walls, whereas the colloids in the latter remain behind.

The filtered sap is heated to 80–90° with milk of lime, to saturate the acids, and precipitate the albuminoid substances. The juice is next saturated with carbon dioxide, phosphoric acid, or SO_2 (arresting fermentation), filtered through animal charcoal, concentrated, and further evaporated in *vacuum pans* to a thick syrup, out of which the solid sugar separates on cooling. The raw sugar obtained in this manner is further purified with a pure sugar solution, in the centrifugal machine, etc.—*refined sugar.*

Sugar may be obtained from the syrupy mother liquor—the molasses, which cannot be brought to crystallization:

(1) By *osmosis*, depending upon diffusion through parchment paper, in apparatus similar to filter presses.

(2) By *washing* (elution) (Scheibler, 1865).

The sparingly soluble saccharates of lime and strontium are obtained from the molasses (see below) and these are freed from impurities by washing with water or dilute alcohol (elution). The purified saccharates are afterwards decomposed by carbon dioxide, and the juice which is then obtained, after the above plan, is further worked up.

The molasses is also worked up into *rum* (p. 122).

Properties.—When its solutions are evaporated slowly cane sugar separates in large monoclinic prisms, and dissolves in ⅓ part water of medium temperature; it dissolves with difficulty in alcohol. Its sp. gr. equals 1.606. Its real rotatory power, A_D, at 20° is +66.5° (B. 17, 1757). Cane sugar melts at 160°, and on cooling solidifies to an amorphous glassy mass; in time this again becomes crystalline and non-transparent. At 190–200° it changes to a brown non-crystallizable mass, called *caramel*, which finds application in coloring liquors.

The quantity of sugar in solution may be determined by polarization, using the apparatus of *Soleil-Ventzke-Scheibler*, or the half-shadow

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* Ein Jahrhundert chemischer Forschung unter dem Schirme der Hohenzollern, von A. W. Hofmann, 1881.

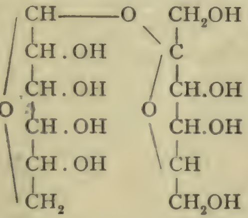
† Statistisches Jahrbuch für das deutsche Reich, herausgegeben von Kaiserlichen statistischen Amt. 14. Jahrgang 1893. S. 24, 174.

‡ Hdb. d. chem. Technologie, Ferd. Fischer, 1893. S. 851–888.

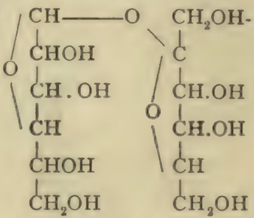
instrument devised by Schmidt and Hänsch (B. **27**, 2282), as well as by means of the *saccharimeter* of Brix.

Transformations and Constitution.—Cane sugar decomposes into d-glucose and d-lævulose (invert sugar) when boiled with dilute acids. Ferments also hydrolyze it. It is only after this occurs that it is capable of reducing Fehling's solution. Mixed with concentrated sulphuric acid it is converted into a black, humus-like body. d-Saccharic acid, tartaric acid and oxalic acid are formed when it is boiled with nitric acid. Cane sugar heated to 160° with an excess of acetic anhydride gives *octacetyl ester*, $C_{12}H_{14}O_3(O . C_2H_3O)_8$. This latter fact and the failure of cane sugar to reduce Fehling's solution under ordinary conditions are made to appear in the following formulas:

I. (Tollens)
(B. **16**, 923)



II. (E. Fischer)
(B. **26**, 2405)



Cane-sugar yields saccharates with the bases. Alcohol will precipitate the *monobasic saccharate*, $C_{12}H_{22}O_{11} . CaO + 2H_2O$. The *tribasic saccharate*, $C_{12}H_{22}O_{11}$. 3CaO, is not readily soluble in water (B. **16**, 2764). Strontium and barium give perfectly similar saccharates (B. **16**, 984) (p. 574). The *tetranitrate*, $C_{12}H_{18}(NO_2)_4O_{11}$, explodes violently.

Milk Sugar, Lactose, *Lactobiose*, $C_{12}H_{22}O_{11} + H_2O$, occurs in the milk of mammals, in the amniotic liquor of cows, and in certain pathological secretions. Fabriccio Bartoletti, of Bologna, discovered it in 1615.

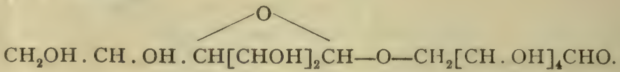
Milk sugar is prepared from whey. This is evaporated to the point of crystallization, and the sugar which separates purified by repeated crystallization.

Milk sugar crystallizes in white, hard, rhombic prisms. It becomes anhydrous at 140°, and melts with decomposition at 205°. It is soluble in 6 parts cold or 2½ parts hot water, has a faint sweet taste, and is insoluble in alcohol. Its aqueous solution is dextrorotatory and exhibits *bi-rotation* (p. 549). It resembles the hexoses in reducing ammoniacal silver solutions; this it effects even in the cold, but in case of alkaline copper solutions boiling is necessary to reach the desired end.

Transformations and Constitution.—Milk sugar yields galactose and d-glucose when it is heated with dilute acids; it ferments with difficulty with yeast, but undergoes the *lactic* fermentation with great readiness (p. 335). Nitric acid oxidizes it to d-saccharic acid and mucic acid.

Bromine water converts it into *lactobionic acid*, $C_{12}H_{22}O_{12}$, which is changed to d-gluconic acid and d-galactose upon digesting it with acids (B. **22**, 362).

Lactose Carboxylic Acid, $C_{12}H_{23}O_{11}.CO_2H$, is produced by the addition of hydrocyanic acid. It decomposes into d-glucoheptonic acid (p. 568) and d-galactose (A. **272**, 198). Compare isosaccharin, p. 537. *Phenyl Lactosazone*, $C_{12}H_{20}O_9(N_2HC_6H_5)_2$, melts at 200° (B. **20**, 829). *Octoacetyl Lactose*, $C_{12}H_{14}O_3[OCO.CH_3]_8$, melts at 95–100° (B. **25**, 1453). These transformations can be understood from the following formula of milk sugar:



$$CH_2OH.CH.OH.\overset{\frown O \frown}{CH[CHOH]_2CH}—O—CH_2[CH.OH]_4CHO.$$

Milk sugar forms crystalline derivatives with the nitrate and sulphate of amidoguanidine (B. **28**, 2614).

Maltose, *Malt Sugar, Maltobiose*, $C_{12}H_{22}O_{11} + H_2O$, is a variety of sugar formed, together with dextrine, by the action of malt diastase (p. 122) upon starch (in the mash of whiskey and beer). It is capable of direct fermentation. It is also an intermediate product in the action of dilute sulphuric acid upon starch, and of ferments (diastase, saliva, pancreas) upon glycogen (p. 578).

Maltose is usually obtained in the form of crystalline crusts, composed of hard, white needles; $[\alpha]_D^{20°} = 137°$ (B. **28**, R. 990), and can be obtained from starch by means of diastase (A. **220**, 209).

Transformations.—It was formerly believed that maltose could be directly fermented by yeast. It appears, however, that there is present a second enzyme (along with invertin, which does not hydrolyze maltose) in the yeast. This (glucase?) decomposes the maltose into glucose (B. **29**, R. 663). It reduces Fehling's solution only in the presence of grape sugar, which it resembles very closely (A. **220**, 220).

Diastase does not exert any further change upon maltose; when boiled with dilute acids, it absorbs water and passes completely into d-glucose or grape sugar. Nitric acid oxidizes it to d-saccharic acid, while chlorine changes it to malto-bionic acid, $C_{12}H_{22}O_{12}$. This yields grape sugar and d-gluconic acid when it is heated with acids.

Hydrocyanic acid transforms it into maltose carboxylic acid, $C_{12}H_{23}O_{11}.CO_2H$, which decomposes into d-glucose and d glucoheptonic acid (A. **272**, 200).

When boiled with lime water, it forms *Isosaccharin* (p. 537). *Octoacet-maltose*, $C_{12}H_{14}O_3(OCO.CH_3)_8$, melts at 156° (A. **220**, 216; B. **28**, 1019). *Phenylmaltosazone* melts at 206° (B. **20**, 831). Maltose and milk sugar possess the same structural formula (B. **22**, 1941).

The following saccharobioses are less important: *Isomaltose*, $C_{12}H_{22}O_{11}$, isomeric with maltose, results from the action of hydrochloric acid upon d-glucose (B. **28**, 3024), and in the mashing process (B. **25**, R. 577); $[\alpha]_D = +70°$ (B. **29**, R. 991). Yeast does not ferment it; diastase converts it into maltose. Its *osazone* melts at 150–153°.

Mycose, $C_{12}H_{22}O_{11} + 2H_2O$, Trehalose (B. **24**, R. 554; **26**, 1332), occurs in several species of fungi—*e. g.*, in *Boletus edulis* (B. **27**, R. 511), in ergot of rye, and in the oriental *Trehala*. Acids convert it into d-glucose (B. **26**, 3094).

Melibiose, $C_{12}H_{22}O_{11}$, is produced in the hydrolysis of melitriose. Further hydrolysis converts it into d-glucose and d-galactose (B. **22**, 3118; **23**, 1438, 3066).

Turanose, $C_{12}H_{22}O_{11}$, a white mass, $[\alpha]_D = +65$ to $+68°$, is formed along with d-glucose in the partial hydrolysis of melezitose. Its *osazone* melts at 215–220° (B. **27**, 2488).

Agavose, $C_{12}H_{22}O_{11}$, is obtained from the stalks of *Agave americana* (B. **26**, R. 189). **Lupeose,** $C_{12}H_{22}O_{11}$, is contained in certain seeds (B. **25**, 2213).

B. TRISACCHARIDES, SACCHAROTRIOSES.

Melitose, *Raffinose,* $C_{18}H_{32}O_{16} + 5H_2O$, *Melitriose* (B. **21**, 1569) $[\alpha]_D = 104°$. It occurs in rather large quantity in Australian manna (varieties of Eucalyptus), in the flour of cotton seeds, in small amounts in sugar beets, and being more soluble than cane sugar, it accumulates in the molasses in the sugar manufacture. From this it crystallizes out with the sugar (A. **232**, 173). Its crystals have peculiar terminal points, and show strong rotatory power (Plus sugar).

To determine the raffinose quantitatively consult B. **19**, 2872, 3116.

By hydrolysis it yields fructose and melibiose (B. **22**, 1678; **23**, R. 103).

Melezitose, $C_{18}H_{32}O_{16} + 2H_2O$, occurs in the juice of *Pinus larix*, and in the Persian manna. It resembles cane sugar very much. It is distinguished from the latter by its greater rotatory power (B. **26**, R 694), and in not being so sweet to the taste. It melts at 148° when anhydrous. It is also a triose (B. **22**, R. 759). It decomposes by partial hydrolysis into d-glucose and turanose (B. **27**, 2488).

Stachyose, $C_{18}H_{32}O_{16}$, is obtained from *Stachys tuberifera* (B. **24**, 2705).

C. POLYSACCHARIDES.

It is very probable that the polysaccharides having the empirical formula $C_6H_{10}O_5$, really possess a much higher molecular weight, $(C_6H_{10}O_5)_n$. They differ much more from the hexoses than the di- and tri-saccharides. They are, as a general thing, amorphous, dissolve with difficulty in water, and lack most of the chemical characteristics of the hexoses. By hydrolysis, that is when boiling them with dilute acids, or under the influence of ferments (p. 519), nearly all are finally broken up into monoses (see dextrine). Their alcoholic nature is shown in their ability to form acetyl and nitric esters. They may be classified as *starches*, *gums* and *cellulose*.

There are certain gums, like cherry gum and beechwood gum, which yield pentoses by hydrolysis. They are, therefore, called *pentosanes* to distinguish them from the *glucosanes*—the polysaccharides, which break down into glucoses when they are hydrolyzed (B. **27**, 2722).

Starches.—(1) *Starch*, Amylum, $(C_6H_{10}O_5)_n$, is found in the cells of many plants, in the form of circular or elongated microscopic granules, having an organized structure. The size of the granules varies, in different plants, from 0.002–0.185 mm. Air-dried starch contains 10–20 per cent. of water; dried over sulphuric acid it retains some water, which is only removed at 100°. Starch granules are insoluble in cold water and alcohol. When heated with water they swell up at 50°, burst, partially dissolve, and form *starch paste*, which turns the plane of polarization to the right. The soluble portion is called *granulose*, the insoluble, *starch cellulose*. Alcohol precipitates a white powder—*soluble starch*—from the aqueous solution. The blue coloration produced by iodine is characteristic of starch, both the soluble variety and that contained in the granules (B. **25**, 1237; **27**, R. 602; **28**, 385, 783). Heat discharges the coloration, but it reappears on cooling. Consult B. **28**, R. 1025, for a quantitative, colorimetric method for the determination of starch.

Boiling dilute acids convert starch into dextrine and d-glucose (Kirchhoff, 1811). When heated from 160–200° it changes to dextrine. Malt diastase changes it to dextrine, maltose, and isomaltose (p. 576) (B. **27**, 293). This is a reaction which is technically conducted on a large scale in the manufacture of alcohol from starch (p. 122).

(2) *Paramylum*, $(C_6H_{10}O_5)_n$, occurs in the infusoria *Euglena viridis*. It is not colored by iodine, and is soluble in potassium hydroxide.

(3) *Lichenine*, $(C_6H_{10}O_5)_n$, moss-starch, occurs in many lichens, and in Iceland moss (*Cetraria islandica*). Iodine imparts a dirty blue color to it. It yields d-glucose when boiled with dilute acids.

(4) *Inulin* is found in the roots of dahlia, in chicory, and in many Compositæ (like *Inula helenium*). Iodine gives it a yellow color. When boiled with water it is completely changed to d-fructose.

(5) *Glycogen*, $(C_6H_{10}O_5)_n$, animal starch, occurs in the liver of mammals. Boiling with dilute acids causes it to revert to d-glucose, and ferments change it to maltose.

The Gums, $(C_6H_{10}O_5)_n$.—These are amorphous, transparent substances widely disseminated in plants; they form sticky masses with water and are precipitated by alcohol. They are odorless and tasteless. Some of them yield clear solutions with water, while others swell up in that menstruum and will not filter through paper. The first are called the *real gums* and the second *vegetable mucilages*. Nitric acid oxidizes them to mucic and oxalic acids.

Dextrine, *Starch Gum*, *Leiocome*.—By this name are understood substances readily soluble in water and precipitated by alcohol; they appear as by-products in the conversion of starch into dextrine, *e. g.*, heating starch alone from 170–240°, or by heating it with dilute sulphuric acid. Different modifications arise in this treatment: *amylodextrine*, *erythrodextrine*, *achroodextrine;* they have received little study (B. **28**, R. 987; **29**, R. 41). They are gummy, amorphous masses, whose aqueous solutions are dextro-rotatory, hence the name dextrine. They do not reduce Fehling's solution, even on boiling, and are incapable of direct fermentation; in the presence of diastase, however, they can be fermented by yeast (p. 122). They are then converted into d-glucose. They yield the same product when boiled with dilute acids. The dextrines unite with phenylhydrazine (B. **26**, 2933). The yeast gum, present in yeast cells, has been isolated (B. **27**, 925).

Dextrine is prepared commercially by moistening starch with two per cent. nitric acid, allowing it to dry in the air, and then heating it to 110°. It is employed as a substitute for gum (B. **23**, 2104).

Arabin Gum exudes from many plants, and solidifies to a transparent, glassy, amorphous mass, which dissolves in water to a clear solution. Gum arabic or gum Senegal consists of the potassium and calcium salts of arabic acid. The latter can be obtained pure by adding hydrochloric acid and alcohol to the solution. It is then precipitated as a white, amorphous mass, which becomes glassy at 100°, and possesses the composition $(C_6H_{10}O_5)_2 + H_2O$. It forms compounds with nearly all the bases; these dissolve readily in water.

Some gum varieties, *e. g.*, gum arabic, yield galactose in considerable quantity when boiled with dilute sulphuric acid; and with nitric acid they are converted into mucic acid; others (like cherry gum) are transformed on boiling with sulphuric acid into l-arabinose, $C_5H_{10}O_5$ (p. 536), and into oxalic acid, not mucic acid, by nitric acid. The gum, extracted from beechwood by alkalies and precipitation with acids, is converted into xylose (p. 536) by hydrolytic decomposition. Hence these gums must be regarded as pentosanes (p. 577) (B. **27**, 2722).

Bassorin, vegetable gum, constitutes the chief ingredient of gum tragacanth, Bassora gum, and of cherry and plum gums (which last also contain arabin). It swells up in water, forming a mucilaginous liquid, which cannot be filtered; it dissolves very readily in alkalies.

Pectine substances (from πήκτος, coagulated) occur in fruit juices, *e. g.*, apple, cherries, etc. They cause these, under suitable conditions, to gelatinize. They are closely allied to the vegetable gums, and may be regarded as oxyvegetable gums (A. **286**, 278; B. **28**, 2609).

Cellulose, $(C_{12}H_{20}O_{10})_x$, *Wood Fibre, Lignose*, forms the principal ingredient of the cell membranes of all plants, and exhibits an organized structure. To obtain it pure, plant fibre or, better, wadding is treated successively with dilute potash, dilute hydrochloric acid, water, alcohol, and ether, to remove all admixtures (incrusting substances). Cellulose remains then as a white, amorphous mass. Fine, so-called Swedish, filter paper consists almost entirely of pure cellulose, which can readily be made very combustible by the addition of nitrocellulose (B. **27**, R. 526).

Cellulose is insoluble in most of the usual solvents, but dissolves without change in an ammoniacal copper solution. Acids, various salts of the alkalies and sugar precipitate it as a gelatinous mass from such a solution. After washing with alcohol it is a white, amorphous powder. Cellulose swells up in concentrated sulphuric acid and dissolves, yielding a paste from which water precipitates a starch-like compound (amyloid), which is colored blue by iodine. After the acid has acted for some time the cellulose dissolves to form dextrine, which passes into grape sugar, when the solution is diluted with water and then boiled. The compound $C_{12}H_{14}O_4(OCOCH_3)_6$, an amorphous mass, is produced on heating cellulose with acetic anhydride to 180°.

Cellulose is used in making paper, oxalic acid (p. 432), parchment paper, gun cotton, smokeless powder, and celluloid.

So-called parchment paper (vegetable parchment) is prepared by immersing unsized filter paper in sulphuric acid (diluted one-half with water) and then washing it with water. It is very similar to ordinary parchment, and is largely employed.

Cold, concentrated nitric acid, or, what is better, a mixture of nitric and sulphuric acids, converts cellulose or cotton into esters or so-called *nitro-celluloses*.

The resulting products exhibit varying properties, depending upon their method of formation. Pure cotton dipped for a period of three to ten minutes into a cold mixture of $1HNO_3$ and $2–3H_2SO_4$, then carefully washed with water, gives gun cotton (pyroxylin). This is insoluble in alcohol and ether or even in a mixture of the two. It explodes violently if fired in an enclosed space, either by a blow or percussion. It burns energetically when ignited in the air, but does not explode. Cotton exposed for some time to the action of a warm mixture of 20 parts pulverized nitre and 30 parts concentrated sulphuric acid becomes *soluble pyroxylin*, which dissolves in ether containing a little alcohol. The solution, termed *collodion*, leaves the pyroxylin, on evaporation, in the form of a thin, transparent film, not soluble in water. It is employed in covering wounds and in photography.

In composition gun cotton is *cellulose hexa-nitrate*, $C_{12}H_{14}(O.NO_2)_6O_4$, whereas the pyroxylin, soluble in ether and alcohol, is essentially a *tetra-nitrate*, $C_{12}H_{16}(O.NO_2)_4O_6$, and a *penta-nitrate*, $C_{12}H_{15}(O.NO_2)_5O_5$ (B. **13**, 186).

Collodion dissolved in nitroglycerol (equal parts) yields explosive gelatine or smokeless powder (B. **27**, R. 537).

Celluloid is a mixture of nitrocellulose and camphor. It is a hard, gummy mass. It possesses the disadvantage, from a technical standpoint, that it burns very energetically when it has been once ignited.

ANIMAL SUBSTANCES OF UNKNOWN CONSTITUTION.

Now that the description of the aliphatic bodies has been concluded, certain substances of animal origin will be mentioned. Their exhaustive treatment properly belongs in the province of physiological chemistry. It is especially noteworthy that very frequently well-known amido-acids of the aliphatic series are found among the decomposition products of these rather enigmatical bodies. Many of the substances described in the following pages occur, both in the vegetable and animal kingdoms, in closely related modifications of uncertain constitution, *e. g.*, the albuminous bodies, the nucleïnes, the cholesterines, the enzymes, etc., and also the *carbohydrates* (p. 572) and *lecithins* (p. 475), which have already received mention.

ALBUMINOUS SUBSTANCES, ALBUMINATES.*

These were formerly known as proteïn substances, and form the principal constituents of the animal organism. They also occur in plants (chiefly in the seeds), in which they are produced exclusively. When absorbed into the animal organism as nutritive matter they sustain but very slight alteration in the process of assimilation.

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* Die Eiweissarten der Getreidearten, Hülsenfrüchte und Oelsamen von H. Ritthausen, 1872. Handbuch der physiologisch- und pathologisch-chemischen Analyse, von F. Hoppe-Seiler, 1893. "Eiweisskörper," Artikel von Drechsel in Ladenburg's Handw., 1885.

The composition of the different albuminous bodies varies within definite limits:

C	50.0 to	55.0	per cent.	Crystallized Albumin:	C	51.48	per cent.
H	6.9 "	7.3	"		H	6.76	"
N	15.0 "	19.0	"		N	18.14	"
O	19.0 "	24.0	"		O	22.66	"
S	0.3 "	2.4	"		S	0.96	"

Stohmann and Langbein (J. pr. Ch. [2] **44**, 345) have calculated the formula $C_{720}H_{1134}N_{218}S_5O_{248}$ for crystallized albumin.

The molecular magnitude of no albuminous substance is definitely known. There is no doubt but that their molecular weights are large. Sabanejeff, employing Raoult's method, obtained 15,000 for the molecular value of purified egg albumen. All albuminous bodies rotate the plane of polarization to the left. They always leave an inorganic residue when they are burned. In the solution and precipitation processes employed in obtaining them free from mineral ash, the albumin frequently sustains a change in its properties (B. **25**, 204).

When boiled with dilute sulphuric or hydrochloric acid, or with baryta water, the decomposition products are, in addition to ammonia and carbon dioxide, mainly amido-acids of the fatty series: glycocoll, leucine, leuceïnes, $C_nH_{2n-4}NO_2$ (unsaturated glycines), aspartic and glutaminic acids, $C_5H_9NO_4$ (p. 493); and diamidocarboxylic acids (p. 481), *e. g.*, $\alpha\varepsilon$-diamidocaproic acid (? lysine, B. **25**, 2456, 3504), as well as β-phenyl-α-amidopropionic acid, tyrosine, etc.

Furthermore, hydrochloric acid and stannous chloride convert albuminous substances into two bases analogous to creatine and creatinine: *Lysatin*, $C_6H_{13}N_3O_2$, and *Lysatinin*. These are said to yield urea when they are decomposed (B. **23**, 3096). *Arginine*, $C_6H_{14}N_4O_2$ (Z. phys. Ch. **21**, 155), should also be added to the list of decomposition products. Concentrated hydrochloric acid is said to have converted albumin into a dihydroxypyridine melting at 295° (B. **29**, 2109, R. 15).

Loew maintains that the production of albumin in plants is due to the condensation of asparagine aldehyde (Pflüger's Arch. **22**, 503).

The putrefaction caused by the activity of lower organisms—bacilli, bacteria, etc.—in albuminous bodies gives rise not only to fatty acids as far as caproic acid, but also to *δ-amidovaleric acid* (p. 359) (B. **24**, 1364). *phenyl-acetic acid*, $C_6H_5CH_2 . COOH$, *β-oxyphenyl-propionic acid*, $HO[4]C_6H_4[1]CH_2 . CH_2 . CO_2H$, *phenol*, C_6H_5OH, *indol*, $C_6H_4\left\{\begin{array}{l}(1)CH\\(2)NH\end{array}\right.\!\!\gg CH$, *skatol* or *β-methyl-indol*, $C_6H_4\left\{\begin{array}{l}(1)C(CH_3)\\(2)NH\end{array}\right.\!\!\gg CH$, *skatol-carboxylic acid*, $C_6H_4\left\{\begin{array}{l}(1)C(CH_3)\\(2)NH\end{array}\right.\!\!\gg C . CO_2H$, and *skatol-acetic acid*, $C_6H_4\left\{\begin{array}{l}(1)C(CH_3)\\(2)NH\end{array}\right.\!\!\gg CCH_2CO_2H$ (B. **22**, 701).

Basic compounds also result in this decomposition. These are the diamines and imines of the paraffin series, and have been called *ptomaines* or *toxines* (p. 310).

Indol and skatol have also been obtained from albumin by the action of caustic potash.

Certain pathogenic micro-organisms, as diphtheria and anthrax bacilli, produce a decomposition that is far more extended, and results in the formation of poisonous substances somewhat similar to albumin and peptone, which have been termed *toxalbumins;* these lose their toxic properties when their aqueous solutions are heated (B. **23**, R. 251).

The nitrogenous derivatives of albumin, voided with urine, can not in general be obtained artificially from the albuminous bodies. The organism, by oxidation and decomposition, changes albumin into an ammonium salt, which is then further synthetically worked up, chiefly in the liver, to urea, uric acid, and other amido-bodies.

The albuminates are usually insoluble in water. Their presence in the juices or fluids of the living organism is entirely due to the presence of salts and other substances, which are but partly understood. They are insoluble in alcohol and ether; most of them are precipitated on boiling in weak acetic acid solution, also by acetic acid and potassium ferrocyanide, or acetic acid and sodium sulphate, and by certain mineral acids, as well as by salts of the heavy metals.

Many albuminous substances are separated from solution by boiling, by alcohol, by mineral acids, etc. They are *coagulated*. Their solubility is entirely changed. This is not the case with the so-called *propeptones*. Propeptone precipitated by alcohol dissolves after the removal of the latter as readily in water as before the precipitation.

Reactions.—All albuminous bodies are colored a violet-red on warming with a mercuric nitrate solution containing a little nitrous acid (this is like tyrosine) (Millon's reagent). A yellow color is produced when they are digested with nitric acid. This becomes a gold yellow on neutralization with ammonia (*Xanthoproteïc reaction*). The albuminous substances yield beautiful violet-colored solutions on digesting them with fuming sulphuric acid. Caustic potash and copper sulphate also impart a red to violet coloration to albuminous solutions (*Biuret reaction*) (B. 29, 1354). On the addition of sugar and concentrated sulphuric acid they acquire a red coloration, which on exposure to the air becomes dark violet. If concentrated sulphuric acid be added to the acetic acid solution of albuminous bodies they receive a violet coloration and show a characteristic absorption band in the spectrum.

The manner of distinguishing and classifying the various albuminous substances is yet very uncertain. The original albumins, occurring in nature, are albumin, globulin, caseïn, gluten proteïns, etc., while the secondary modifications obtained from them through the agency of chemicals or ferments are: acidalbumins, albuminates, coagulated albumins, fibrins, propeptones, peptones, etc.

Many of these modifications result from the breaking-down of the molecule of the original albumin. It is well worth noting in such instances that the decomposition product still maintains the essential character of the albuminous substances just as the starch molecules yield molecules of grape sugar, which, like the starch, continue as carbohydrates. The breaking-down of the original albumin, in the reactions referred to, is proved by the astonishing fall in molecular weight. This has been partly determined by the method of Raoult (p. 32) and in part by testing the electric conductivity (Skand. Arch. Physiolog. 5, 337). The decomposition is also evidenced by the fact that the proportion of the carbon to the nitrogen in the decomposition product frequently varies from that in the other decomposition product, just as much as it varies between these substances in the parent body (Schmiedeberg, Arch. exp. Path. 39). This decomposition of the albumin molecule is a hydrolytic decomposition. See albumin substances, p. 583.

In a certain number of secondary albumin modifications ammonia, sulphur, and amido-acids, like leucine and tyrosine, etc., have been split off, without the loss of the essential character of the albumin.

Of pre-eminent importance is the fact that the organs of the living animal body have the power of synthesizing the original albumin from the products with lower molecular weights. This is certainly similar to the formation of glycogen—the animal starch, from grape sugar, in the liver.

Many substances, not all of which have heretofore been classed as albuminous substances, split off sugar when treated with acids; they are therefore glucosides* (Z. physiolog. Ch. **12**, 389).

1. **Albumins,** soluble in water, dilute acids and alkalies, dilute and saturated solutions of sodium chloride or magnesium sulphate. *Coagulated by heat.* Serum-, egg-, milk-, and vegetable albumin belong in this class. Nitrous acid converts egg albumin into yellow **desamido-albumin.** This is still digestible. It does not show the biuret reaction (B. **29**, 1354).

2. **Globulins,** insoluble in water, but soluble in dilute solutions of sodium chloride and magnesium sulphate. These solutions are coagulated on boiling. Magnesium sulphate at 30° precipitates them without any alteration in properties. This class contains: **Myosin** (muscles), **fibrinogen** (in the living blood), changing under the influence of fibrin ferment to fibrin; **fibrin globulin,** obtained from fibrin by means of trypsin; **serum globulin**; *crystal-lens globulin* and *vitellin* (in the yellow of the egg).

3. **Caseïns.**—Milk caseïn behaves in general like an albuminate (see under 6), but is distinguished by the fact that whey enzyme precipitates it in neutral or feebly acid solutions in the presence of soluble calcium compounds. This is not the case with the albuminate (B. **29**, R. 913). The caseïn of milk appears also to be combined with a phosphorus-containing body, *e. g.*, with **nucleïn.** For this reason some writers class caseïn with the nucleo-albumins.

Caseïns also occur in plants.

4. The **Gluten Proteïns** are characterized by their physical properties. In the hydrous state they are pasty, elastic masses. They only occur in wheat flour. Here they constitute the chief essential for bread-making. Gluten is insoluble in water, and sparingly soluble in water containing a very little dilute acid or alkali. Its solubility in alcohol (60–70 volume per cent.) is very characteristic. Some gluten proteïns when decomposed yield large quantities of glutaminic acid. Thus, Ritthausen, obtained not less than 25 per cent. of glutaminic acid from **mucedin.**

5. **Acid Albumins** or **Syntonins** are *insoluble in water* and salts, soluble in hydrochloric acid or a soda solution, *do not expel carbonic acid* from calcium carbonate, and are precipitated in *acid* solution by neutral metallic salts of the alkalies and alkaline earths. Caustic alkali converts them into albuminate. The acid albumins are produced on treating the albumins, globulins, etc., with hydochloric acid, or with other acids (B. **28**, R. 858).

6. **Albuminates,** *insoluble in water* and salts, readily soluble in dilute acids and a soda solution, *expel carbonic acid* from calcium carbonate. They can be precipitated without alteration from acid, as well as *alkaline*, solutions by saturation with solutions of neutral salts of the alkalies and alkaline earths. The albuminates are produced when albumin, globulin, etc., are treated with caustic alkali.

7. **Coagulated Albuminous Substances.**—They are insoluble in water and salt solutions, and scarcely soluble in dilute acids. They are obtained by heating other albumins, or by the addition of alcohol, certain mineral acids and metallic salts.

8. **Fibrins,** *insoluble in water*, scarcely soluble in a salt solution, and in other salts, or in dilute acids, formed from globulin by a ferment in discharged blood. The process of blood coagulation is expressed according to the investigations of Schmiedeberg (Arch. exp. Path. **31**, 8) by the following equation:

$$\underset{\text{Fibrinogen}}{(C_{111}H_{168}N_{30}SO_{35})_2} + H_2O = \underset{\text{Fibrin}}{C_{108}H_{162}NO_{30}SO_{34}} + \underset{\text{Fibrinoglobulin.}}{C_{114}H_{176}N_{30}SO_{37}}.$$

9. **Propeptones or Albumoses** (B. **29**, R. 518). Certain modifications are produced by the action of the enzymes of the gastric juice or pepsine upon the albuminous bodies. This is largely due to the hydrolytic decomposition induced in the process of digestion. They can be precipitated by a saturated ammonium sulphate solution at 30°, and also at higher temperatures. "The albumoses cannot be coag-

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* The Physiology of the Carbohydrates, by Pavy.

ulated either by boiling their neutral or acidulated aqueous solutions, nor by the prolonged action of alcohol upon them, although they are insoluble in strong alcohol, and are precipitated by the latter." *

They are partly soluble in water, and partly insoluble. They resemble the albumins and globulins very much, and by prolonged digestion they finally pass into—

10. **Peptones**, which are perfectly soluble in water, acids, alkalies and salts of the light metals. They cannot be separated from their solutions either by heat, nitric acid, by acetic acid and ferrocyanide of potassium, or by ammonium sulphate. Phosphotungstic acid frequently precipitates the peptones in the presence of hydrochloric acid, mercuric chloride, basic lead acetate, alcohol, etc., incompletely.

The albuminous substances, when acted upon by *pepsine* and dilute hydrochloric acid at 30–40°, are dissolved, completely digested, and at first are converted into *syntonins* or *acid albumins*, then into *albumoses* or *propeptones*, and finally into so-called *peptones*, which dissolve readily in water, are not coagulated by heat, and are not precipitated by most reagents (B. **16**, 1152; **17**, R. 79). For the molecular weight and constitution of the peptones consult B. **25**, R. 643; **26**, R. 22. The enzyme of pancreas and the ferments of decay produce real peptone from albumin. It is noteworthy that albumin is changed by water above 100°, best in the presence of a small quantity of a mineral acid, into albumoses and peptone. It is very certain that the peptones result from the hydrolytic decomposition of albumin, and in the organism again revert to coagulable albumin.

There is also a series of bodies more or less closely related to albumin; some are of a more complex structure than albumin itself, because they are albumin compounds. Others show the character of a more or less advanced stage of decomposition of the albumin molecule. In the first class we find:

(*a*) The albumin glucosides. These have received mention. Then follows the large family of mucus bodies—*e. g.*, the group of *mucin*, of *mucinogen*, of *mucoïds*, and of the *hyalogens*. These represent compounds of the albuminous substances with the carbohydrates.

(*b*) **Nucleïn.**—This occurs in cell-nuclei. It yields albumin and *nucleïc acids* by hydrolysis. These are found in the *nucleïn bases*, such as xanthine, guanine, adenine, hypoxanthine, and even sometimes carbohydrates, linked in an ether-like form very probably with phosphoric acid. The very varying composition of the nucleïns would indicate a large family, which would attach itself to the so-called nucleoalbumins. See B. **27**, 2215, for the decomposition of *nucleïc acid* (*adenylic acid*) by acid.

(*c*) *Hæmoglobin* possesses great importance from a physiological standpoint. It has been pretty thoroughly studied chemically.

HÆMOGLOBINS.

The *oxyhæmoglobins* are found in the arterial blood of animals and may be obtained in crystalline form from the blood corpuscles by treatment with a solution of sodium chloride and ether, and the addition of alcohol. The different oxyhæmoglobins, isolated from the blood of various animals, exhibit some variations, especially in crystalline form. Their elementary composition approximates that of albumin very closely. It differs, however, by an iron content of 0.4 per cent. If the molecular weight of hæmoglobin be calculated on the supposition that it contains an atom of iron, the value obtained exceeds 13,000. The hæmoglobins are bright red, crystalline powders, very soluble in cold water, and are precipitated in crystalline form by alcohol. When the aqueous solution of oxyhæmoglobin is placed under the air-pump or when it is exposed to the agency of reducing agents (ammonium sulphide) it parts with oxygen and becomes *hæmoglobin*. The latter is also present in venous

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* Lehrbuch der phys. Chemie von R. Neumeister, S. 229 (1897).

blood, and may be separated out in a crystalline form (B. 19, 128). Its aqueous solution absorbs oxygen very rapidly from the air, and reverts again to oxyhæmoglobin. Both bodies in aqueous solution exhibit characteristic absorption spectra, whereby they may be easily distinguished.

If carbon monoxide be conducted into the oxyhæmoglobin solution, oxygen is also displaced and hæmoglobin-carbon monoxide formed. This can be obtained in large crystals with a bluish color. This explains the poisonous action of carbon monoxide. The bluish-red solution of hæmoglobin-carbon monoxide shows two characteristic absorption spectra. These do not disappear upon the addition of ammonium sulphide (distinction from oxyhæmoglobin).

On heating to 70°, or through the action of acids or alkalies, oxyhæmoglobin is split up into albuminous bodies, fatty acids and the dye-stuff *hæmatochromogen*, which in contact with free oxygen changes to *hæmatin*, which in a dry condition is a dark brown powder. It contains 9 per cent. of iron, and, as it appears, corresponds to the formula, $C_{34}H_{34}FeN_4O_5$.

The addition of a drop of glacial acetic acid and very little salt to oxyhæmoglobin (or dried blood) aided by heat, produces microscopic reddish-brown crystals of hæmin (hæmatin hydrochloride), $C_{32}H_{31}N_4O_3FeCl$ (B. 29, 2877); alkalies separate hæmatin, $C_{32}H_{31}N_4O_3FeOH$, again from it. The production of these crystals serves as a delicate reaction for the detection of blood.

The great physiological importance of hæmoglobin is evident from the fact that in the lungs it removes the oxygen from inhaled air, holds it loosely combined, and passes it over to the various organs in the course of circulation—that is, it renders the oxidation processes possible by transferring oxygen to them. Hydrogen bromide converts hæmin into *Hæmatoporphyrin*, $C_{16}H_{18}N_2O_3$ (Nencki and Sieber, B. 21, R. 433). This is closely allied to *Phylloporphyrin*, $C_{16}H_{18}N_2O$. This is obtained by fusing *phyllocyanin* with caustic soda. *Chlorophyll* treated with concentrated acids yields *phyllocyanin*. The absorption spectra of the neutral and acid solutions of both bodies are identical, and only differ in that "the lines of hæmato-porphyrin are moved a shade toward the red." The two bodies probably bear the same relation to each other that are observed existing between purpurine and oxyanthraquinone. That is, they are different stages of oxidation of one and the same nucleus substance (E. Schunck and L. Marchlewski, A. 290, 306; B. 29, 2877). This kinship corresponds to an analogous physiological action. Consequently hæmoglobin attracts free oxygen and surrenders it in the organs when it is required, whereas chlorophyll liberates oxygen from carbonic acid and water in order to present it to the living animal. As the lower fungi, *without* chlorophyll, are capable of building up carbohydrates, fats, and albumins from many molecules which contain the groups CH_2 and CHOH, there seems to be no doubt that synthetic work can be executed by the living cell substance to which (in the green portion of plants) the requisite atomic groups are presented by processes of reduction (privately communicated by E. Pflüger).

The following substances are produced by the decomposition of albuminous bodies. They still retain the albumin character, but in a somewhat modified form:

GELATINOUS TISSUES AND GELATINES.

These are mostly nitrogenous, organized substances, which on boiling with water are converted into gelatines (glue).

Glutin, gelatine, swells up in cold water, and on boiling dissolves to a thin lævorotatory solution, which gelatinizes on cooling. By the addition of concentrated acetic acid or protracted boiling with a little nitric acid, the solution loses the property of gelatinizing (liquid gelatine). Tannic acid precipitates from the aqueous solution gelatine tannate, a yellowish, glutinous precipitate. The substances yielding gelatine combine also with tannic acid, withdrawing the latter completely from its solutions and forming *leather*.

Glycocoll, leucine, and other amido-fatty acids are the principal substances produced on boiling gelatine with dilute sulphuric acid or alkalies. When glutin is heated with hydrochloric acid on a water-bath there results a glutin-peptone chlorhydrate, soluble in anhydrous methyl and ethyl alcohol. The **glutin peptones** can be obtained from it. Dry distillation produces pyrrol and pyridine bases (bone-oil). Glutin peptone contains, as shown by its behavior with nitrous acid, at least three different kinds of N-atoms. One of these exists as NH_2, the second as NH, and the third as a tertiary N-atom (B. **29**, 1084).

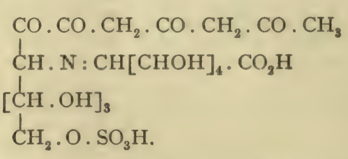
Alcoholic hydrochloric acid changes gelatine into a compound that nitrous acid converts into a substance, $C_5H_6N_2O_3$, very similar to the diazo fatty-acids. It may be that it represents **diazo-oxyacrylic ester**, $CN_2 : C(OH) . CO_2 . C_2H_5$ (B. **19**, 850).

Although glutin in its composition is very similar to albumin, it cannot replace the specific functions of albumin in the animal metabolism.

Bone-, fat-, and cartilaginous tissues are produced according as certain substances are arranged in their gelatinous parts by lime and magnesium salts, or by fats, etc.

Chondrin results on boiling ordinary cartilage. It is a mixture of glutin and certain compounds of chondroït-sulphuric acid with gelatine and albuminous bodies on the one side and alkalies on the other (Schmiedeberg: Arch. exp. Pathol. und Pharmakol. **28**).

Schmiedeberg represents the constitution of chondroït-sulphuric acid as follows:



$$\begin{array}{l} CO.CO.CH_2.CO.CH_2.CO.CH_3 \\ | \\ CH.N:CH[CHOH]_4.CO_2H \\ | \\ [CH.OH]_3 \\ | \\ CH_2.O.SO_3H. \end{array}$$

The acid is very probably a condensation product of sulphuric acid, acetic acid, glycuronic acid and glucosamine. Artificial mixtures of glutin and salts of chondroït-sulphuric acid give the reactions of so-called chondrin.

Chitin belongs to the class of substances present in bone cartilage. It is the chief component of the shells of crabs, lobsters, etc. It is interesting to observe that its nitrogen exists as *glucosamine* (p. 550), because Ledderhose (Z. phys. Ch. 2, 224) has demonstrated that when chitin is decomposed with hydrochloric acid glucosamine and acetic acid result. Hence, Schmiedeberg believes that the following equation has value:

$$\underset{\text{Chitin}}{C_{18}H_{30}N_2O_{12}} + 4H_2O = \underset{\text{Glucosamine}}{2C_6H_{13}NO_5} + \underset{\text{Acetic Acid.}}{3CH_3.CO_2H.}$$

Chitin heated to 184° with molten alkali yields acetic acid and *chitosan*, which breaks down into acetic acid and glucosamine when it is heated with hydrochloric acid (B. **28**, 82). The shell substance of the fungi is probably identical with chitin, and the **Mycosin**, obtained from it by means of caustic potash, is identical with chitosan (B. **28**, 821, R. 476).

The following are probably disintegrated albumin molecules:

Elastin, which differs from albumin in containing less sulphur.

Ceratin, horn substance, is the principal ingredient of hair, nails, etc. It contains a variable but at times a very high sulphur content (0.7 to 5.0 per cent.) (B. **28**, R. 561). Notwithstanding it approximates the percentage composition of albumin very closely, ceratin gives almost the same decomposition products as albumin, *e.g.*, *leucine* and *tyrosine*.

UNORGANIZED FERMENTS OR ENZYMES.

Unorganized ferments playing an important part in fermentation, in many processes of decay, and in digestion, appear to be closely related to the albuminous substances. They are soluble in water. Boiling water destroys their activity. Enzymes are the cause of the hydrolysis of glucosides, and in fermentation their rôle appears to be the decomposition of the polysaccharides, which are to be regarded as glucosides. The configuration of the glucosides (B. **28**, 984, 1429) exercises a very definite influence upon the action of the enzyme. The following are of vegetable origin: *Invertin*, *diastase* (p. 120), *emulsin* or *synaptase*, present in bitter almonds, *myrosin*, found in mustard seeds, *papaïn*, etc. In the digestive juices of animals we have *pytaline* (πτύαλος, saliva) in the saliva, *pepsin* (πεπτός, digested) in the gastric juice, and other enzymes.

BILIARY SUBSTANCES.

In the bile, the liquid secretion of the liver, which effects the emulsion and reabsorption of the fats, occur the sodium salts of two peculiar acids, **glycocholic** and **taurocholic**; also **lecithin** (p. 475), **cholesterine** and **bile pigments**—bilirubin, biliverdin. Various views prevail in regard to the origin of the latter. The relationship to the albuminous bodies has never been determined.

Cholalic Acid, $C_{24}H_{40}O_5$ (B. **27**, 1339; **28**, R. 332; **29**, R. 142), melting at 195°, when anhydrous, is a monobasic acid. It is obtained together with *glycocoll* as a decomposition product of glycocholic acid, and with *taurine* as a product of the decomposition of taurocholic acid. Glyco- and taurocholic acids exist as sodium salts in the bile. In preparing cholalic acid, *choleïnic acid*, $C_{24}H_{40}O_4$, and *fellinic acid*, $C_{23}H_{38}O_4$, have been discovered. It forms a blue compound with iodine, quite similar to that given by starch and iodine (B. **28**, 783; R. 720). When oxidized with potassium permanganate it yields not only acetic acid, but also o-phthalic acid (B. **29**, R. 346).

Taurocholic Acid, $C_{24}H_{39}O_4 . NH . CH_2 . CH_2 . SO_3H$ (ταῦρος, ox; χολή, gall), is very soluble in water and alcohol, and when boiled with water breaks up into cholalic acid and taurine (p. 306).

Glycocholic Acid, $C_{24}H_{39}O_4 . NH . CH_2 . CO_2H$, melts at 133°, or boiled with alkalies it decomposes into glycocoll and cholalic acid (p. 354).

Cholesterine, $C_{27}H_{45} . OH$, is a monohydric alcohol, occurring not only in the bile, but in the blood, in the brain, and in the yolk of eggs, also in wool-fat. It is soluble in alcohol, crystallizes in mother-of-pearl leaflets, containing $1H_2O$, and possessing a fatty feel. It parts with its water of crystallization at 100°, melts at 145°, and distils at 360° with scarcely any decomposition. It crystallizes from ether in prisms.

Cholestene, $C_{27}H_{26}$, melting at 90° (B. **27**, R. 301), is formed by the reduction of its chloride. See B. **29**, R. 906, for the oxidation products of cholesterine.

Lanoline, obtained from raw sheeps' wool, contains esters of cholesterine and isocholesterine (melting at 138°) with the higher fatty acids. It is applied as a salve, as it will take up water and is absorbed by the skin.

The soaps resulting from the saponification of lanoline were found to contain *Lanoceric Acid*, $C_{30}H_{60}O_4$, melting at 104°, *Lanopalminic Acid*, $C_{16}H_{32}O_3$, melting at 87°, myristic acid (p. 250), and *Carnaubaic Acid*, $C_{24}H_{48}O_2$ (B. **29**, 2890).

Substances similar to cholesterine have also been detected in plants. *Phytosterine*, isomeric with cholesterine, is present in plant seeds and sprouts (B. **24**, 187). *α*- and *β-Amyrines* (B. **24**, 3836) obtained from *elemiresin*, as well as *lupeol* (B. **24**, 2709), present in seed shells of *Lupinus Luteus*, are similar to cholesterine.

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